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Errata.—1948—*Vol. I, No.* 2.

The figure number and subtitle of the diagram on page 64 (incorrectly labelled Fig. 1) should be interchanged with those of the diagram on page 69 (incorrectly labelled Fig. 3).

THE COMPOSITION OF THE SEED AND FUNICLE OILS OF *ACACIA CYCLOPS*

by

M. M. BLACK, D. A. HARRIS and H. M. SCHWARTZ

OPSOMMING

'n Monster van die saadolie en twee monsters van die funikelolie van *Acacia cyclops* is ondersoek. Die vet inhoud van die saad en van die funikel is respektiewelik 9·95 persent en 40·6 persent.

Die fisiese en chemiese konstante van die olies is bepaal, asook die vetsuursamestelling. Die jodiumwaarde van die saadolie (136·9) was baie hoër as dié van die funikelolies (71·9 – 73·1). Hierdie verskil is ook waar te neem in die vetsuursamestelling van die olies. Die vetsuursamestelling (bereken as gewigspersentasies) van die saad- en funikelolies was respektiewelik: lauriensuur—spoor, spoor; miristiensuur—0·7, 0·3 – 0·4; palmitiensuur—5·6, 19·1 – 21·6; steariensuur—0·6, 2·7 – 4·0; arakidiensuur—0·8, 0·4 – 0·7; C_{23-24} versadigde sure—2·9, niks; tetradecenoïensuur—niks, spoor; heksadecenoïensuur—8·6, 7·3 – 9·3; oliensuur—10·1, 60·5 – 61·7; linolsuur—67·7, 2·5 – 3·1; linoleensuur—0·8, spoor; C_{20} onversadigde sure—2·1, 1·2 – 3·5.

Die onverseepbare deel van die saad- en funikelolie is gedeeltelike ondersoek. Dit bevat 19 persent van 'n mengsel van karotinoide, waarvan die identiteit nie vasgestel is nie.

SUMMARY

A sample of the seed oil and two samples of the funicle oil of *Acacia cyclops* have been examined. The fat content of the seed and of the funicle is 9·95 and 40·6 per cent respectively.

The physical and chemical constants of the oils have been determined, together with the fatty acid composition. The iodine value of the seed oil (136·9) was much higher than that of the funicle oils (71·9 – 73·1)' This difference was reflected in the fatty acid composition of the oils. The component fatty acids (weights per cent) of the seed and funicle oils respectively were: lauric acid—trace, trace; myristic acid—0·7, 0·3 – 0·4; palmitic acid—5·6, 19·1 – 21·6; stearic acid—0·6, 2·7 – 4·0; arachidic acid—0·8, 0·4 – 0·7; C_{23-24} saturated acids—2·9, nil; tetradecenoic acid—nil, trace; hexadecenoic acid—8·6, 7·3 – 9·3; oleic acid—10·1, 60·5 – 61·7; linoleic acid—67·7, 2·5 – 3·1; linolenic acid—0·8, trace; C_{20} unsaturated acids—2·1, 1·2 – 3·5.

A partial examination of the unsaponifiable fractions of the seed and funicle oils was made. The unsaponifiable fraction of the funicle oil contains 19 per cent of a mixture of carotenoids, the identity of which was not established.

Acacia cyclops is a large shrub belonging to the sub-family Mimosoideæ of the family Leguminosæ. It is a native of Australia and was introduced into South Africa to serve as an anchorage for the windswept soil of the Cape Flats. It has become well established in the Cape Peninsula and has spread along the south-east coast of South Africa as far as Port Elizabeth. It is of no economic importance. *Acacia cyclops* is easily distinguished from closely related species such as *A. saligna* (Port Jackson willow) and *A. melanoxylon* by the fact that the seeds are attached to the pod by large, scarlet, fleshy funicles which surround the seeds in a double fold. The funicle contains about 40 per cent of deep red oil which has a very much lower iodine value than the seed oil. Since the occurrence of seeds with large funicles or arils is not common, very few funicle oils have been examined. It was felt, therefore, that it would be of interest to determine the composition of *Acacia cyclops* funicle oil and compare it with that of the seed oil.

Extraction of oils

The seeds were collected during December, January or February. Seeds with bleached or orange-coloured funicles were rejected.

Approximately 100 g. of seeds and funicles were separated by hand and the oil content of seeds and funicles determined separately by extraction with petroleum ether (b.p. 60°C. – 80°C.) in a Soxhlet extraction apparatus for 18 hours.

Larger samples of oil for component acid analysis were obtained as follows: It was found that the seeds, which have hard black shells, are practically impervious to hot acetone or petroleum ether, provided the shells are not broken. The funicles, on the other hand, readily yield their oil. It was possible, therefore, to extract funicle oil, uncontaminated by seed oil, by extraction of the seeds with their attached funicles with petroleum ether or acetone. When the extraction of the funicle oil was complete, the funicles were colourless or pale lemon in colour and were brittle and could be separated from the seeds by winnowing. The seeds were then milled to a fine meal and the seed oil extracted with petroleum ether. Approximately 300 g. each of funicle and seed oil were extracted by this method from seeds collected during 1947, petroleum ether being used as solvent. A sample of funicle oil was also extracted in 1945 using acetone as solvent. The acetone was removed by distillation, the oil taken up in ether and the ethereal solution washed with water to remove gums and water-soluble materials. The ether was finally removed by distillation. The yields and analytical characteristics of the funicle and seed oils extracted in this way agreed very closely with those of the oils extracted from the separated seeds and funicles.

General characteristics of the oils

The average weight of 100 seeds and funicles, the oil yields and the general analytical characteristics of the seed and funicle oils are shown in Table I. The funicle oil is deep red in colour, whereas the seed oil has a light greenish-yellow colour. The most important difference between the constants of the funicle oils and the seed oil is in the iodine value which is 72 – 73 in the case of the funicle oils and 136·9 in the case of the seed oil.

TABLE I

(i) *Weights and oil contents of* Acacia cyclops *seeds and funicles.*

Average weight of 100 seeds with attached funicles		5·25 g.
Average weight of 100 seeds		3·43 g.
Average weight of 100 funicles		1·82 g.
Oil in seeds	9·95 per cent.	Based on weight of seed + funicle = 6·5 per cent
Oil in funicles	40·6 per cent.	Based on weight of seed + funicle = 14·1 per cent

(ii) *Characteristics of the oils.*

	Funicle oil		*Seed oil*
	1945 *crop*	1947 *crop*	1947 *crop*
Specific gravity, 25°/25°	0·917	0·916	0·922
Refractive index (25°C.)	1·4691	1·4726	1·4746
Saponification value	188·5	187·4	186·3
Iodine value	71·9	73·1	136·9
Acid value	3·25	3·20	2·26
Unsaponifiable matter, per cent	2·78	3·18	0·99

Component acids of the seed and funicle oils

The component acids of the sample of funicle oil extracted in 1947 were determined by subjecting the lead salts of the mixed fatty acids to recrystallization from alcohol[1].

The "liquid" and "solid" acids so obtained were converted to their methyl esters and fractionated in an electrically heated and packed column. Selected fractions were examined spectro-photometrically at 234 mμ after isomerization with alkali under the conditions laid down by Hilditch, Morton and Riley[2] in order to determine their content of methyl linoleate. The result of the component acid analysis is given in Table II.

The component acids of the seed oil and of the sample of funicle oil extracted during 1945 were determined by subjecting the mixed fatty acids to low temperature crystallization from acetone and ether. The procedure used in the two cases differed because of the difference in the iodine value of the mixed acids.

Examination of the funicle oil by the lead-salt crystallization method had indicated that the composition of the fatty acids was similar to that of neatsfoot oil examined by Hilditch and Shrivastava[3]. The conditions used by these authors, therefore, were employed in the crystallization of the funicle oil fatty acids. The acids (274·1 g.) were recrystallized first from ether (10 ml. per g.) at −40°C. The deposited acids (70·1 g., iodine value 15·9) were recrystallized under the same conditions when 57·5 g. (Fraction A, iodine value 3·4) separated. The soluble acids obtained from this recrystallization were combined with those obtained from the first crystallization and crystallized from acetone (10 ml. per g.) at −60°C. when 190·8 g. (Fraction B, iodine value 86·0) were deposited leaving 26·6 g. (Fraction C, iodine value 115·9) in solution. The results of the recrystallization of the funicle oil are summarized in Table III.

The conditions employed in the crystallization of the seed oil acids were those recommended by Hilditch and Riley[4] for fats in which oleic and linoleic acid are the major components. The acids (193·9 g.) were first recrystallized from acetone (5 ml. per g.) at −30°C. 40·6 Gram were deposited, leaving 153·3 g. (Fraction C, iodine value 158·4) in solution. The deposited acids were further crystallized from ether (10 ml. per g.) at −30°C. when 24·67 g. (Fraction A, iodine value 31·8) were deposited and 15·90 g. (Fraction B, iodine value 144·4) left in solution. Data relating to the recrystallization of the seed oil acids are summarized in Table V.

The various fractions obtained by low temperature crystallization were converted into the corresponding methyl esters and fractionally distilled. Selected fractions were subjected to alkali isomerization under the appropriate conditions and examined spectrophotometrically at 234 mμ and 268 mμ. The computed composition of the various fractions of funicle and seed oil acids are shown in Tables IV and VI respectively. The final results of the component acid analyses of the seed oil and the two samples of funicle oil are collected together in Table VII.

The relative merits of low temperature crystallization and chemical (*e.g.* lead salt) methods of resolution of fatty acid mixtures have been discussed by Hilditch[5]. Comparison of the data in Tables II, III and IV shows that in the case of the funicle oils, low temperature crystallization gave a very much better separation of the saturated and unsaturated fatty acids than did the lead salt separation. The final results of the analyses by the two methods, however, show reasonably good agreement.

Hexadecenoic acid was found to be present in appreciable amount in both the funicle oils and the seed oil. Unfortunately insufficient material was available to attempt to isolate and identify the acid. Evidence for its occurrence rests on the following data:—

Of the esters derived from Fraction B of the funicle oil acids (1945 sample), the first three distilled fractions had the following characteristics:—

Fraction	*Sap. eq.*	*Iodine value*	$E_{1\ cm.}^{1\ per\ cent}$ 234 mμ (*after alkali isomerization*)
R.F.O. B_1	269·1	50·0	—
B_2	289·0	76·9	5·4
B_3	290·6	79·1	6·4

In the case of the 1947 sample of funicle oil, the first three fractions distilling from the "liquid" esters had the following characteristics:—

Fraction	*Sap. eq.*	*Iodine value*
R.F.O. L_1	275·3	64·0
L_2	282·2	64·9
L_3	290·7	84·4
	(C_{18} esters had S.E. 295·9 I.V. 88·5)	

The composition of these fractions can only be computed on the assumption that they contain substantial amounts of hexadecenoic acid. Similarly it is only possible to compute the composition of the following fractions distilled from the methyl esters of Fractions B and C of the seed oil acids on the assumption that they contain methyl hexadecenoate:—

	Sap. eq.	*Iodine value*	$E_{1\ cm.}^{1\ per\ cent}$ 234 mμ (*after alkali isomerization*)	$E_{1\ cm.}^{1\ per\ cent}$ 268 mμ (*after alkali isomerization*)
R.S.O. B_1	286·0	138·6	594	—
B_2	289·0	141·8	617	—
C_1	283·0	143·4	644	—
C_2-C_{15}	291·3	155·8	668	5·3

DISCUSSION

As far as the authors are aware, the only funicle or aril fats which have been examined are the aril fats of *Myristica fragrans* and *Myristica malabarica*[6] and the fat from the aril of the traveller's palm (*Ravenala madagascariensis*[7]. The chemical constants of these fats are similar to those of the funicle oil of *Acacia cyclops*, as will be seen from the figures given below:—

Aril fat from	*Iodine value*	*Saponification value*
Myristica fragrans	78 – 80	170 – 173
Myristica malabarica	51 – 53	189 – 191
Ravenala madagascariensis	61·2	185·6

The component fatty acids present in these fats have unfortunately not been determined. Funicle and aril fats are classified as "fruit coat fats" by Hilditch in his monograph on "The Chemical Constitution of the Natural Fats"[8]. The composition of *Acacia cyclops* funicle oil may be compared, therefore, with that of more common fruit coat fats which are derived from the pericarp and receptacle of the plant. A general feature of the composition of this class of fats is that in nearly all cases the major component acids include only palmitic and oleic acids with occasionally linoleic acid[9]. *Acacia cyclops* funicle oil is a typical member of the class since its major component acids (Table VII) are oleic acid (60 per cent) and palmitic acid (20 per cent) together with a smaller proportion of hexadecenoic acid (7 – 9 per cent).

The marked difference in iodine value of the funicle and seed oils of *Acacia cyclops* is reflected in the difference in composition of the oils (Table VII). In the funicle oil unsaturation is due mainly to oleic acid and to a lesser extent to hexadecenoic acid. Linoleic acid occurs only to the extent of 2 – 3 per cent. The higher unsaturation of the seed oil is due to its greatly enhanced content of linoleic acid which constitutes 67·7 per cent of the total acids. The content of oleic acid is reduced to 10·2 per cent but that of hexadecenoic acid (8·6 per cent) is much the same as in the funicle oil. The funicle oil also contains a higher proportion of saturated acids than the seed oil. Differences such as these between the composition of the fruit coat and seed fat from the same plant are common[9], since seed fats contain a wide variety of specific fats according to their botanical origin, whereas fruit coat fats, as has been mentioned above, almost invariably contain only palmitic and oleic acids as their major components.

TABLE II

Component acids of A. cyclops *funicle oil* (1947 *crop*) (*by preliminary lead salt separation*).

	"Solid" acids	*"Liquid" acids*	*Total (excluding unsaponifiable matter)*
Weight (g.)	91·0	159·0	250·0
Per cent (wt.)	36·4	63·6	100·0
Iodine value	40·4	83·3	67·7
Component acids per cent (*wt.*):			
Myristic	0·4	—	0·4
Palmitic	14·9	4·2	19·1
Stearic	4·0	—	4·0
Arachidic	0·7	—	0·7
Hexadecenoic	3·5	5·8	9·3
Oleic	12·5	48·0	60·5
Linoleic	0·4	2·1	2·5
C_{20} unsaturated	—	3·5	3·5

TABLE III

A. cyclops *funicle oil* (1945 *crop*)
(*Low temperature crystallization of acids.*)

Fraction	*Weight* (g.)	*Per cent total*	*I.V.*	$E^{1\ per\ cent}_{1\ cm.}$ 234 mμ (*after alkali isomerization*)
A. Insoluble in ether (10 ml./g.) at −40°C. ..	57·5	20·9	3·4	—
B. Insoluble in acetone (10 ml./g.) at −60°C.	190·8	69·4	86·0	10·6
C. Soluble in acetone (10 ml./g.) at −60°C.	26·6	9·7	115·9	243

TABLE IV

A. cyclops *funicle oil* (1945 *crop*)
Component fatty acids.

Component acids (*increments per cent wt.*)	*A*	*B*	*C*	*Total* (*excluding*) *unsaponifiable matter*)
Lauric	—	—	0·5	0·5
Myristic	0·2	—	0·1	0·3
Palmitic	17·0	4·5	0·1	21·6
Stearic	2·7	—	—	2·7
Arachidic	0·4	—	—	0·4
Tetradecenoic ..	—	—	0·9	0·9
Hexadecenoic ..	—	6·6	0·7	7·3
Oleic	0·6	57·5	3·6	61·7
Linoleic	—	0·6	2·5	3·1
Linolenic	—	—	0·3	0·3
C_{20} unsaturated ..	—	0·2	1·0	1·2

TABLE V

A. cyclops *seed oil*
Low temperature crystallization of acids.

Sample	*Weight* (g.)	*Total per cent*	*I.V.*	$E^{1\ per\ cent}_{1\ cm.}$ 234 mμ (*after alkali isomerization*)	$E^{1\ per\ cent}_{1\ cm.}$ 268 mμ (*after alkali isomerization*)
A. Insoluble in ether (10 ml./g.) at −30°C.	24·7	12·7	31·8	—	—
B. Insoluble in acetone (5 ml./g.) at −30°C.	15·9	8·2	144·4	632	—
C. Soluble in acetone (5 ml./g.) at −30°C.	153·3	79·0	158·4	692	5·7

TABLE VI

A. cyclops *seed oil*
Component fatty acids.

Component acids (increments per cent wt.)	*A*	*B*	*C*	*Total (excluding unsaponifiable matter)*
Lauric	—	—	0·1	0·1
Myristic	0·3	—	0·4	0·7
Palmitic	5·2	0·4	—	5·6
Stearic	0·6	—	—	0·6
Arachidic	0·8	—	—	0·8
Behenic	2·2	—	—	2·2
Lignoceric	0·7	—	—	0·7
Hexadecenoic ..	0·2	0·7	7·7	8·6
Oleic	0·6	1·2	8·3	10·1
Linoleic	1·6	5·8	60·3	67·7
Linolenic	—	—	0·8	0·8
C_{20} unsaturated ..	0·5	0·1	1·5	2·1

TABLE VII

Comparison of component acids (weights per cent) of funicle oils and seed oil.

	Funicle oil		*Seed oil*
	1947 *sample (lead salt separation)*	1945 *sample (low temperature crystallization)*	1947 *sample (low temperature crystallization)*
Lauric	—	0·5	0·1
Myristic	0·4	0·3	0·7
Palmitic	19·1	21·6	5·6
Stearic	4·0	2·7	0·6
Arachidic	0·7	0·4	0·8
$C_{22} - C_{24}$ saturated ..	—	—	2·9
Tetradecenoic	—	0·9	—
Hexadecenoic	9·3	7·3	8·6
Oleic	60·5	61·7	10·1
Linoleic	2·5	3·1	67·7
Linolenic	—	0·3	0·8
C_{20} unsaturated	3·5	1·2	2·1

The unsaponifiable fraction of the seed and funicle oils

The deep red pigment of the funicle oil passed into the unsaponifiable fraction and appeared to be a carotenoid. It was felt, therefore, that it would be of interest to examine this fraction further.

The unsaponifiable fraction was isolated by the S.P.A. method[10]. The methods used for the determination of sterols, α-glyceryl ethers, squalene and saturated hydrocarbons have been described in a previous communication[11]. The unsaponifiable fraction of the funicle oil was dissolved in cyclohexane solution and examined spectrophotometric-

ally using a Beckman quartz spectrophotometer. Absorption maxima were observed at 450 mμ ($E^{1\ per\ cent}_{1\ cm.}$ 484) and 478 mμ ($E^{1\ per\ cent}_{1\ cm.}$ 498) together with an inflection at 500 – 505 mμ. Partition of the unsaponifiable matter between petroleum ether and 90 per cent aqueous methyl alcohol and chromatography on magnesium oxide indicated that the carotenoid fraction consisted of at least three components which were present in approximately equal proportions. No further attempt to isolate and identify the individual carotenoids was made.

If the carotenoids present in the unsaponifiable fraction are calculated as β-carotene ($E^{1\ per\ cent}_{1\ cm.}$ 450 mμ = 2,500 in cyclohexane solution) they are found to make up 19·3 per cent of the fraction. The sterol content of the unsaponifiable fraction was 3 per cent and the glyceryl ether content 1 per cent (Table VIII). The nature of the remainder of the unsaponifiable fraction was not determined.

The unsaponifiable fraction of the seed oil was also analysed. The results are shown in Table VIII. The carotenoid content of the unsaponifiable matter of the seed oil was negligible. The content of sterols and saturated and unsaturated hydrocarbons only account for 56 per cent of the fraction. It was not possible to determine the nature of the other components as the amount of unsaponifiable matter available was insufficient.

TABLE VIII

Composition of the unsaponifiable fraction of the funicle and seed oils.

	Funicle oil per cent	*Seed oil per cent*
Carotenoids (as β-carotene) ..	19	Nil
Sterols	3	50
α-glyceryl ethers	1	Nil
Squalene	—	1
Saturated hydrocarbons	—	5

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THE ALKALOID FROM THE FRUIT OF *SOLANUM PANDURÆFORME E. MEY*

by

D. P. VELDSMAN and P. G. J. LOUW

OPSOMMING

'n Gliko-alkaloïed met smeltpunt 276°C. – 280°C. (ontbinding) en molekulêre formule $C_{45}H_{73}O_{16}N$ is uit die vruggies van *Solanum panduræforme* geïsoleer. Die suiker-komponente van die alkaloïed is as *d*-glukose, *d*-galaktose en *l*-ramnose vasgestel, terwyl die aglikoon van die basis die molekulêre samestelling van $C_{27}H_{43}O_3N$ het en by 250°C. – 252°C. (ontbinding) smelt.

Derivate van die alkaloïed en sy aglikoon is berei en met die van solasonien en solasodien vergelyk.

Die alkaloïed wat uit die vruggies van *Solanum panduræforme* berei is, is naverwant aan maar nie identies met solasonien nie.

SUMMARY

A glyco-alkaloid with m.p. 276°C. – 280°C. (decomp.) and molecular formula $C_{45}H_{73}O_{16}N$ was isolated from the berries of *Solanum panduræforme*. The sugars were identified as *d*-glucose, *d*-galactose and *l*-rhamnose, while the aglycone of the base melted at 250°C. – 252°C. (decomp.) and had the molecular formula $C_{27}H_{43}O_3N$.

Derivatives of the base and its aglycone were prepared and compared with those of solasonine and solasodine.

The alkaloid from the fruit of *Solanum panduræforme* was found to be closely related to, but not identical with, solasonine.

Solanum panduræforme is well known in South Africa and occurs in widespread areas throughout the Union. It is generally known as the "bitter apple" or "gifappel". The fruit (apples) of the plant are very tempting to children and cause serious poisoning. The fruit is also used as a remedy for ringworms in animals.

Steyn[1] described the symptoms and post-mortem appearances caused by per os dosing of the ripe and green fruit to rabbits. The experiments confirm the evidence that the fruits contain a very active ingredient.

On working up the extract obtained by means of hot alcohol, a colourless, crystalline alkaloid with m.p. 276°C. – 280°C. (decomposition) was obtained. Hydrolysis of this glyco-alkaloid with 2 per cent sulphuric acid gave the aglycone with melting-point 250°C. – 252°C. (decomp.) and an equimolecular mixture of the three sugars, glucose, rhamnose and galactose.

On account of the close relationship of this alkaloid with the alkaloid solasonine isolated by several independent workers from other Solanum species, its properties are summarized comparatively with those of solasonine. Briggs and his colleagues gave a thorough survey of the properties of solasonine and of the chemical investigation of the Solanum species from which solasonine was isolated[2, 3, 4, 5].

In 1930 Levi[2] isolated a glyco-alkaloid from the fruit of *Solanum aviculare*. Both the base and its aglucone, however, were obtained as amorphus powders only and of the derivatives prepared, only the thiocyanate was obtained as a crystalline compound. Bell and Briggs reinvestigated this species and isolated a colourless, crystalline glyco-alkaloid, m.p. 284°C. – 285°C. (decomp.) which after further investigation proved to be solasonine.

The melting point of the alkaloid from Sol. panduræforme was nearly coincident with that of solasonine. Authentic samples of solasonine and solasodine were kindly presented to us by Prof. Briggs, to whom our thanks are due. This sample of solasonine had a m.p. of 276°C. – 280°C. on the Kofler micro-melting point apparatus. (The

m.p. determined with the electrically heated copper block, according to Briggs, was 283°C. – 284°C.) A mixed m.p. of solasonine and the new alkaloid showed no depression. According to the experience of Bell and Briggs[2], however, mixed melting points do not seem valid criteria of identification in this series of alkaloids.

The aglycone of the base of Sol. panduræforme differed from solasodine in m.p., 250°C. – 252°C. for the former as against 200·5°C. – 201°C. for the latter. A similar difference was observed with solasodine and solauricidine[3] (m.p. of latter is 222°C. – 223°C.), a mixed melting point of these two genins showing no depression. The same applied to the mixed melting point determination of solasodine and the aglucone of the base of Sol. panduræforme—the mixture commenced to melt at 185°C. (m.p. of sample of solasodine 185°C. – 197°C.).

It may be worth mentioning that solasodine and solauricidine are closely related in their physical and chemical properties. Bell and Briggs could not find any structural differences between these two alkaloids.

Table I summarizes the properties of the alkaloids isolated from Sol. aviculare, Sol. sodomeum, Sol. auriculatum and Sol. panduræforme.

Colour reactions

Solasonine and solasodine showed a close relationship with the glyco-alkaloid and aglycone of Sol. panduræforme as regards the colour reactions with specific colour reagents as given below:—

Reagent	*Unknown glyco-alkaloid*	*Solasonine*
1. Warm alcohol + conc. H_2SO_4.	Greenish-yellow fluorescence.	Greenish-yellow fluorescence.
2. Acetic acid + conc. H_2SO_4.	Intense red colour.	Intense red colour.

Reagent	*Aglycone of glyco-alkaloid*	*Solasodine*
1. Acetic acid + conc. H_2SO_4.	Intense red colour.	Intense red colour.
2. Warm alcohol + conc. H_2SO_4.	Greenish-yellow colour.	Greenish-yellow colour.
3. Resorcinol + glacial acetic acid + conc. H_2SO_4.	A red/brown green fluorescence at the interface. Shake and heat—a reddish-brown colour with violet fluorescence.	Greenish-yellow colour. Brown/green fluorescence — pinkish red/green fluorescence—light brown/slight green fluorescence.

It is concluded, therefore, that the glyco-alkaloid from Sol. panduræforme is closely related to solasonine in both physical and chemical properties. At this stage, however, there is enough evidence that the glyco-alkaloids are not identical. No particular name, however, is suggested for this new glyco-alkaloid from Sol. panduræforme.

In a physiological test* performed on rabbits it was found that when a 2 per cent solution of the glyco-alkaloid in citric acid solution (equivalent amount citric acid) is injected subcutaneously the M.L.D. is 2·4 ml./kg. Per os it is 23·5 ml./kg. A post-mortem showed ascites, hyperemea of lungs, heart in diastole and the urine bladder empty. The solution has a strong hæmolitic action on the blood of sheep.

* Test by Dr. T. Adelaar, Section of Toxicology, Onderstepoort, to whom our thanks are due.

TABLE I

	Sol. aviculare	*Sol. auriculatum*	*Sol. panduraeforme*
M.p. of glyco-alkaloid	284°C. – 285°C. (decomposition)	270°C. (decomposition)	276°C. – 280°C. (decomposition)
Molecular formula for glyco-alkaloid	$C_{45}H_{73}O_{16}N$	do.	do.
Specific rotation of glyco-alkaloid ..	$[\alpha]W = -68{\cdot}7°$ (alcohol)	——	$[\alpha]W = -73{\cdot}0°$ (abs. alcohol)
Picrate of glyco-alkaloid	m.p. 197°C.	m.p. 185°C.	m p. 180°C. – 185°C.
Picrolonate of glyco-alkaloid	m.p. 231°C.	m.p. 232°C.	m.p. 200°C. – 201°C.
Aglycone of glyco-alkaloid	m.p. 197°C. – 198·5°C.	m.p. 220°C. – 223°C.	m.p. 250°C. – 252°C. (decomp.)
Molecular formula of aglycone ..	$C_{27}H_{43}O_2N$	do.	do.
Sugars	Rhamnose, galactose, glucose	do.	do.
Aglycone-picrate	m.p. 144°C.	141°C.	145°C.
Aglycone-picrolonate	m.p. 232°C.	232°C.	Sinters at 185°C., melts at 218°C. – 220°C.
Diene of aglycone	m.p. 169·5°C. – 170·5°C.	——	218°C. – 223°C.
Bromide of aglycone	m.p. 302°C.	——	280°C.
Sulphate of aglycone	m.p. 293°C.	——	275°C. (decomposition)

EXPERIMENTAL

General method of extraction

Ripe and unripe berries of Solanum panduræforme, collected in the Onderstepoort area, were cut up and dried in front of a fan when the colour of the berries changed to black. The dried material was ground and extracted with hot 95 per cent alcohol. The extract was fanned down to dryness, the residue taken up in 2 per cent acetic acid (or citric acid) and the active principle precipitated by addition of a 5 per cent ammonium-hydroxide solution to the hot solution. The precipitate which appeared white at first and darkened when dried, was separated by centrifuging. It was dissolved in acetic acid and reprecipitated with ammonia and the process repeated once more.

The dried precipitate which still had a brownish-black colour was dissolved in hot 95 per cent alcohol and a quantity of animal charcoal added. The solution was refluxed for about 10 minutes and filtered. After a second decolorization with charcoal, the solution had a deep brown colour. The solution was concentrated, water added (about 20 per cent by volume) and left to crystallize. At first the glyco-alkaloid was obtained as a jelly but after a second crystallization from 80 per cent dioxan-water, it crystallized out in thin blades, arranged in the shape of a cone.

After repeated recrystallization from 80 per cent dioxan-water and finally from 80 per cent methanol, the crystals melted at 276°C. – 280°C. (decomp.).

Properties of the glyco-alkaloid

The glyco-alkaloid from S. panduræforme crystallized from 80 per cent alcohol or 80 per cent dioxan-water in thin plates (or blades) arranging themselves in cone-shaped masses. It melted at 276°C. – 280°C. (decomp.)*.

Solubility

The glyco-alkaloid was found to be very soluble in ethanol, dioxan, methanol, acetic acid, pyridine, amyl alcohol (hot), cyclohexanol, *n*-butyl alcohol and iso-butyl alcohol. In petrol ether, chloroform, benzene, amyl alcohol (cold) it was slightly soluble and insoluble in water, ether, ethyl acetate and acetone.

Specific rotation

0·500 Gram of the glyco-alkaloid was dissolved in 25·0 ml. absolute alcohol, a 1 dm. tube being used.

$$[\alpha]_D^{23^\circ} = -73{\cdot}0^\circ.$$

Molecular weight (Rast)

The glyco-alkaloid was not soluble enough in camphor to permit the molecular weight determination by this method.

Molecular formula†

Found: C, 60·3; H, 8·8; N, 1·55. $C_{45}H_{73}O_{16}N.\frac{1}{2}H_2O$
requires C, 60·6; H, 8·4; N, 1·6 %.

Derivatives of the alkaloid

Picrate

0·5 Gram of the glyco-alkaloid and 0·5 g. picric acid was refluxed in alcoholic solution for half an hour. The picrate was precipitated with excess of ether and crystallized from acetone. The picrate crystallized in thin, yellow needles with m.p. 180°C. – 185°C.

* All melting points done on Kofler micro-melting point apparatus.
† All analyses by Drs. G. Weiler and F. B. Strauss, Oxford, England.

Picrolonate

Hot alcoholic solutions of the glyco-alkaloid and picrolonic acid were mixed and the picrolonate crystallized from 50 – 60 per cent alcohol. The picrolonate crystallized in thin blades with m.p. 200°C. – 201°C.

Found: C, 53·2; H, 7·4; N, 5·8. $C_{55}H_{81}O_{21}N_5.5H_2O$
requires C, 53·35; H, 7·4; N, 5·7 %.

Hydrolysis of the glyco-alkaloid

10 Gram Solanum glyco-alkaloid was dissolved in excess of 2 per cent sulphuric acid and heated in a boiling waterbath for 8 hours. On cooling the sulphate of the aglycone separated. The precipitate was filtered off and the filtrate heated for two more hours. After cooling a further small amount of sulphate separated.

The filtrate was treated with excess barium carbonate and left for half an hour with intermittent shaking. The barium sulphate and barium carbonate was filtered off and the filtrate concentrated. This solution was utilized for identification of the sugar components.

A small amount of the aglycone-sulphate was crystallized from 80 per cent alcohol. The sulphate had m.p. 275°C. (decomp.).

For the preparation of the free aglycone the sulphate was suspended in 5 per cent ammonium hydroxide and heated on a waterbath for 4 hours. The aglycone separated, was filtered off and crystallized from 80 per cent alcohol. After five recrystallizations and decolorization with animal charcoal the aglycone crystallized in thin blades with m.p. 250°C. – 252°C. (decomp.).

Properties of aglycone

Optical rotation of aglycone

0·2714 Gram was dissolved in 25 ml. pyridine, a 1 dm. tube being used.

$$[\alpha]_D^{30^\circ} = -40{\cdot}5^\circ.$$

Found: C, 78·4; H, 10·5; N, 3·4. $C_{27}H_{43}O_2N$
requires C, 78·4; H, 10·3; N, 3·7 %.

Derivatives of aglycone

Aglycone picrate

The preparation was carried out in a similar manner to that of the glyco-alkaloid. The picrate crystallized from dilute alcohol and had m.p. 145°C.

Aglycone picrolonate

The preparation was the same as for the picrate of the aglycone. It crystallized from 60 per cent alcohol in thin blades which softened at 185°C. and melted at 218°C. – 220°C.

Bromo-derivative

The bromo-derivative was prepared in glacial acetic acid solution according to the method of Briggs[2]. The product on crystallization from a mixture of water, alcohol and acetone, containing a small amount of hydrogen bromide, had m.p. 280°C.

Dehydration of the aglycone

0·2 Gram of the aglycone was dissolved in 20 ml. methanol and dry hydrogen chloride passed into the solution until the mixture increased in weight by 20 per cent. The solution became brown. It was left overnight in the refrigerator. The hydrochloride of the dehydration product was precipitated with excess of water and crystallized

from dilute alcohol when it melted at 251°C. – 254°C. (decomp.). The hydrochloride was suspended in 5 per cent ammonium hydroxide and refluxed for half an hour on the waterbath. The diene had m.p. 218°C. – 223°C. (decomp.).

Identification of sugars

An aliquot portion of the sugar solution was evaporated almost to dryness, triturated with absolute alcohol and left for several days. Large crystals of *l*-rhamnose separated with m.p. 92°C. – 93°C. 10 Milligrams of the crystals and 10 mg. *p*-nitrophenylhydrazine were dissolved in 1 ml. hot 95 per cent alcohol and the solution boiled down to about 0·5 ml. and cooled. Yellow crystals separated with m.p. 191°C. – 192°C., which corresponded with that of *l*-rhamnose—*p*-nitrophenylhydrazone. It is concluded, therefore, that *l*-rhamnose was one of the sugar components.

A further aliquot of the sugar solution was heated with phenylhydrazine and glacial acetic acid on the waterbath. After half an hour the solution was diluted with water and heating continued for another half an hour. The yellow crystals which separated were filtered off and washed with 2 per cent acetic acid. After successive trituration with ether and acetone the residue was crystallized from acetone and had m.p. 208°C. – 210°C. which proved the presence of *d*-glucose or an analogous sugar.

Attempts to prove the presence of the third sugar component as galactose with the use of *o*-tolylhydrazine were unsuccessful. Resort, therefore, was taken to the technique of paper partition chromatography[6].

The sugar solution was introduced as circular spots (about 3 – 4 μl. for one drop) in a horizontal line, ruled about 5 cm. from the top of a strip of Whatman No. 1 filter paper. The filter paper was suspended in a glass cylinder (provided with a tightly-fitting glass lid) so that its top end was just hanging into a solution of phenol, saturated with water, in the bottom of the cylinder. The strip was irrigated with the solution for 18 hours overnight. Then the solvent was driven off from the paper in an oven at 100°C., the position of the solvent boundary being marked before transfer to the oven. In order to reveal the position of the sugar spots, the paper was sprayed rapidly and evenly with a mixture containing equal parts of silver nitrate solution (0·1N.) and ammonia solution (5N.) and the strip replaced in the oven for 5 – 10 minutes. The sugar components appeared as dark brown spots on a light brown ground. By this procedure, three components were established in the hydrolysate of the glyco-alkaloid. The three spots, having R_F-values [R_F = (distance moved by solute)/(distance moved by advancing front of liquid)] of 0·39, 0·44 and 0·59, corresponded with those of *d*-glucose, *d*-galactose and *l*-rhamnose respectively.

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RICINOLEIC ACID

II. SOME PHYSICAL PROPERTIES INCLUDING POLYMORPHISM

by

F. HAWKE

OPSOMMING

'n Paar fisiese eienskappe van gesuiwerde monsters risinoleïensuur is bepaal, en is soos volg: $d_{4^\circ}^{25^\circ}$ – 0·9417; $[n]_D^{25^\circ}$ – 1·4703; $[\alpha]_D^{25^\circ}$ – +7·79°. Die suiwer suur skyn in drie polimorfiese vorms voor te kom met smeltpunte 5·0°C., 7·7°C. en 16·0°C. en oorgangstemperature 6·0°C. en 7·2°C. Die waardes soos deur die huidige skrywer bepaal word vergelyk met dié van ander werkers.

SUMMARY

Some physical properties of purified samples of ricinoleic acid have been determined and found to be as follows: $d_{4^\circ}^{25^\circ}$ – 0·9417; $[n]_D^{25^\circ}$ – 1·4703; $[\alpha]_D^{25^\circ}$ – +7·79°. The pure acid appears to exist in three polymorphic forms with melting points of 5·0°C., 7·7°C. and 16·0°C., the transition temperatures being 6·0°C. and 7·2°C. The values determined by the present author are compared with those of other investigators.

There is considerable doubt regarding the purity of specimens of ricinoleic acid isolated in past years[1] and in most cases in which physical properties have been determined the criteria of purity published have been inadequate[2, 3, 4]. The present author reported[5] the isolation of samples of purity greater than 99·1 per cent from castor oil fatty acids.

PHYSICAL PROPERTIES

The physical properties recorded herein were determined on the above samples at a temperature of 25°C. within a week of their preparation. Except when determinations were being carried out the samples were stored in a refrigerator at 6°C. to 7°C. to ensure that no intermolecular reactions took place. The results of these determinations, together with previously published values, are presented in Table I.

TABLE I

	t°C.	$d_{4^\circ}^{t^\circ}$	$[n]_D^{t^\circ}$	$[\alpha]_D^{t^\circ}$
Walden[2]	22°	—	—	+6·67°
Straus *et al.*[4]	21°	0·9450	1·47164	+7·86°
Brown and Green[6] ..	27·4°	0·940	1·4697*	—
Present author	25°	0·9416	1·4703	+7·79°

* t = 20°C.; no mention made of wavelength of light used.

Previously published values for the density vary from 0·940 ($d_{4^\circ}^{27\cdot4^\circ}$)[6] to 0·9450 ($d_{4^\circ}^{21^\circ}$)[4]. Using a temperature coefficient of −0·00068 per degree Centigrade[7, 8], these values become 0·9416 and 0·9423 respectively when converted to a temperature of 25°C.

Using a temperature coefficient of −0·00038 per degree Centigrade[9, 10], similar conversion of published refractive indices to that at 25°C. gives values from 1·4678[6] to 1·4701[4]. Straus *et al.*[4] reported the molecular refraction to be $[M]_D = 88\cdot32$, while that found by the present author was 88·47. The corresponding exaltations are 0·40 and 0·55 respectively: in the present author's opinion these may be due to the proximity of the hydroxyl group to the double bond.

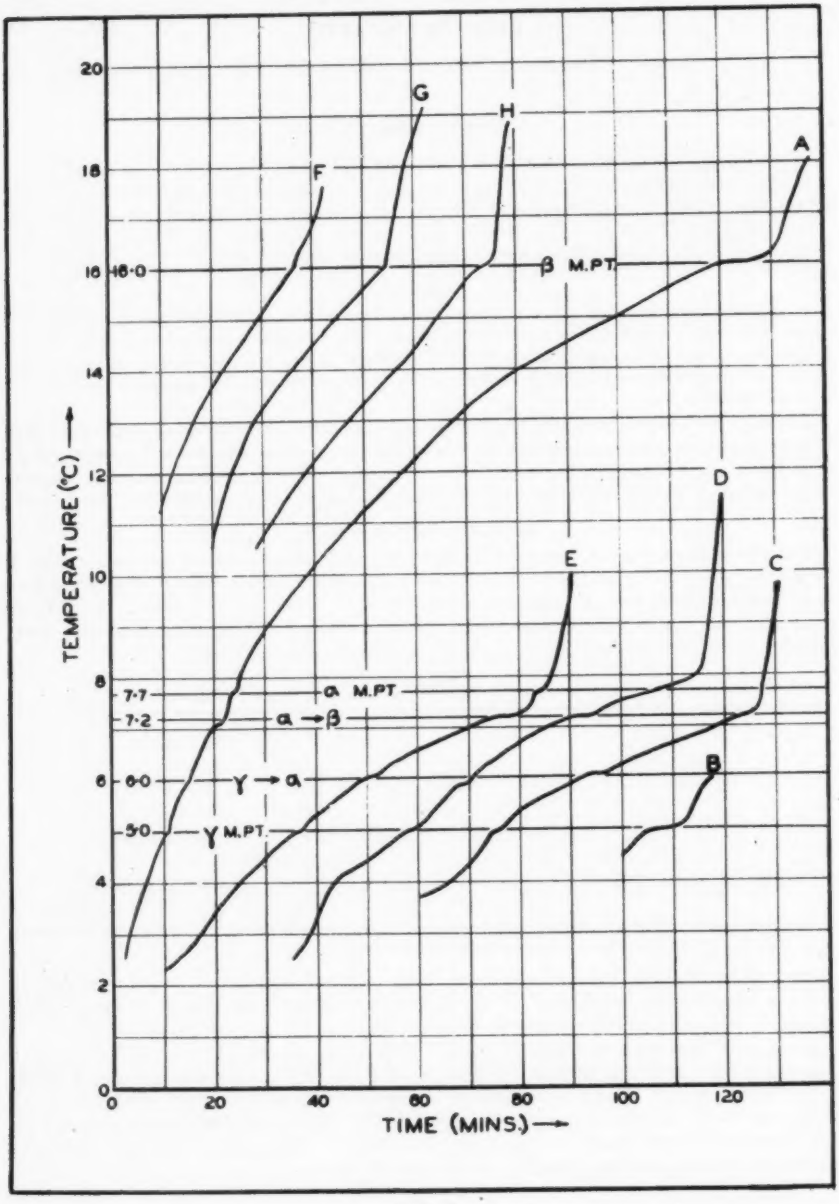
TEMPERATURE (°C)
TIME (MINS.)
β M.PT.
α M.PT
α → β
γ → α
γ M.PT.
18·0
7·7
7·2
6·0
5·0
A
B
C
D
E
F
G
H

FIG. 1.

No precise data are available for the conversion of the optical rotation from one temperature to another, but from values published for methyl ricinoleate[4] it appears that the temperature coefficient is negative and of the *order* of 0·1° per degree Centigrade. Using this coefficient the optical rotation reported by Straus *et al.*[4] becomes approximately +7·5° at 25°C. These latter authors base their claim to have isolated pure ricinoleic acid very largely upon the fact that the value they obtained is higher than any published previously. While agreeing that the optical rotation is the physical constant most affected by the presence of impurities, the present author considers that the value reported by Straus *et al.* indicates that the mate.ial they used was insufficiently pure.

Figures for the optical rotation of solutions of ricinoleic acid in acetone have been published[2, 6], but these are of little value due to insufficient data regarding the concentrations of the solutions used.

Melting points and polymorphism

Straus, Heinze and Salzmann[4] report that ricinoleic acid is dimorphous and give the melting points as 6°C. to 8°C. and 15°C. to 17°C. These values are to some extent corroborated by the findings of other workers, since melting points published lie within two comparatively narrow ranges of 4°C. to 5·5°C.[3, 6] and 15°C. to 17°C.[2, 11].

Using the capillary tube method, the present author found the melting point to lie between 8·2°C. and 8·5°C., the determinations being carried out after the samples had been stored at 6°C. to 7°C. overnight.

Straus *et al.*[4] claim that when a melt of the higher melting form of the acid is rapidly chilled to −30°C. to −40°C., the higher melting form again crystallizes out, but for this to occur the presence of minute seed crystals would appear to be necessary. The present author chilled a number of samples in capillary tubes to −35°C., but found that, on removal from the bath, the acid melted, re-solidified and melted again. This indicated the presence of two polymorphic forms, the transition temperature being higher than the melting point of the low-melting form. Using the technique described by Clarkson and Malkin[12], the melting point of the low-melting form was found to be 5·0°C.

The results of these experiments, together with previously published data, indicated ricinoleic acid to be trimorphous, though there remained the possibility that the values lying between 6°C. and 8°C. might be due to the simultaneous presence of two forms. A further factor to be considered is the possibility of errors in the melting point occasioned by the use of the capillary tube method which has been shown to be inaccurate especially in the case of long chain compounds (*vide* Markley[13]).

To confirm the presence of three forms of ricinoleic acid heating and cooling curves were plotted. The former proved to be most informative: cooling curves showed only the lowest melting point owing to the very marked tendency of ricinoleic acid to supercool. A number of heating curves are shown in Fig. 1, from which the presence of three polymorphic modifications can readily be seen. Using the terminology of Ferguson and Lutton[14], the information presented in Fig. 1 can be summarized as follows:—

γ-melting point	5·0°C.
$\gamma \rightarrow \alpha$ transition temperature	6·0°C.
$\alpha \rightarrow \beta$ transition temperature	7·2°C.
α-melting point	7·7°C.
β-melting point	16·0°C.

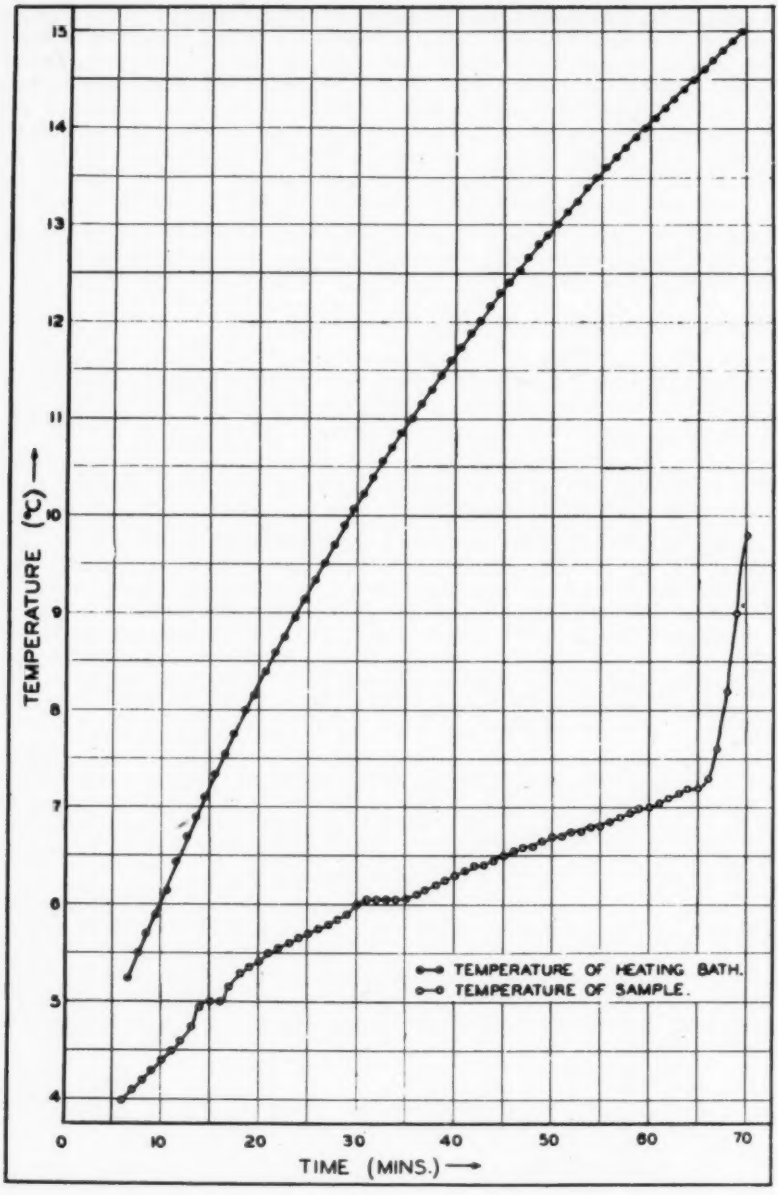
TEMPERATURE (°C) ⟶
TIME (MINS.) ⟶
TEMPERATURE OF HEATING BATH.
TEMPERATURE OF SAMPLE.
15
14
13
12
11
10
9
8
7
6
5
4
0
10
20
30
40
50
60
70

FIG. 2.

EXPERIMENTAL

Values for the physical constants presented above represent the means of at least four determinations on two samples of ricinoleic acid. Temperatures were maintained at 25°C. ± 0·05°C.

The method used in obtaining the data for the thermal curves was similar to that described by Clarkson and Malkin[12]. An "Anschutz" thermometer of low heat capacity was used in place of a thermocouple, the sample weight being 2·0 to 2·5 grams.

Referring to Fig. 1, curve A was obtained by the very slow heating of a sample in which crystallization had been induced by chilling rapidly to 0°C., followed by storage at 2·5°C. for 15 hours.

The melting point of the lowest-melting form is most clearly shown in curve B, in which case the sample was chilled rapidly to −30°C. and then allowed to warm slowly to 4·5°C. Curve C was obtained from a sample which had been cooled from 16°C. in an hour, while curves D and E resulted from slow cooling to about 2°C., followed by storage at the lower temperature for 15 to 20 hours.

The effect of rate of heating on the β-melting point arrest is shown in curves F and G, both of which were obtained from samples in which crystallization had been induced by cooling to 0°C. In order to fix the β-melting point accurately curve H was obtained from a solid sample which had been maintained at 7·3°C. to 7·5°C. for half an hour.

Since the inclusion of all points on the curves in Fig. 1 would tend to be confusing, a specimen curve (C) has been re-plotted on a larger scale in Fig. 2, in which all points are shown. The time-temperature curve for the heating bath has been plotted on the same axes.

The author records his thanks to Professor H. Stephen for his interest and encouragement throughout the course of this investigation.

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GESUBSTITUEERDE KARBAMATE AS MOONTLIKE INSEKDODENDE MIDDELS

deur

A. IMMELMAN en J. P. DE WIT

SUMMARY

The preparations for 20 substituted di-phenyl-carbamates are described. These compounds have been biologically tested and the 2-methyl-3 : 5-dinitro-; 4-nitro-; 4-phenyl-bi-phenyl-carbamate and the bi-phenyl-carbamyl-chloride proved most active, the toxicity of the 4-phenyl compound approaching that of DDT.

OPSOMMING

Die bereiding van 20 gesubstitueerde di-feniel-karbamate word beskrywe. Hierdie verbindings was almal biologies uitgetoets en die 2-metiel-3 : 5-di-nitro-; 4-nitro-; 4-feniel-di-feniel-karbamaat en die di-feniel-karbamiel-chloried het belowende resultate gelewer. Die giftigheid van die 4-feniel verbinding was van dieselfde orde as die van DDT.

Vir geruime tyd is dit reeds bekend dat sekere uretane fisiologiese aktiwiteit besit van een of ander aard[1, 2].

Dit hou dus die moontlikheid in dat die chloor-, nitro-, metiel-, en metoksie-derivate van uretane insekdodende eienskappe mag besit.

Hierdie reeks uretane is dan ook berei met die doel om hulle uit te toets vir enige giftige eienskappe waaroor hulle mag beskik.

As eerste reeks van uretane wat berei sou word, is gekies, die derivate van die fenielester van difenielkarbamiensuur. Die uitgangsmateriaal was deurgaans difenielkarbamiel-chloried wat dan verester kan word met die verskillende gesubstitueerde fenole.

Weens die feit dat difenielkarbamielchloried nie verkry kon word nie is dit as volg berei:—

Bereiding van difenielkarbamielchloried

Die difenielkarbamielchloried (Ph_2NCOCl) is verkry deur fosgeen te lei deur 'n chloroformoplossing van difenielamien, by kamertemperatuur[3].

$$(C_6H_5)_2=N-H + Cl-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow (C_6H_5)_2=N-\overset{\overset{O}{\|}}{C}Cl + (C_6H_5)_2NH.HCl$$

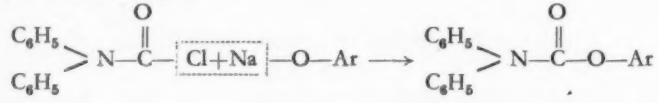
Die fosgeen is ontwikkel deur chloroform te drup in 'n chroom-swawelsuur oplossing wat verhit word op 'n waterbad. Baie beter produksie is verkry deur die oplossing sterk te roer.

Die helfte van die difenielamien gaan verlore as die hidrochloried, wat uitsak uit die kloroformoplossing en afgefiltreer word na verloop van die reaksie.

Die reaksie is eksotermies en indien fosgeen vinnig deurgelei word is dit raadsaam om die reaksiemengsel met ys af te koel. Na afloop van die reaksie word die chloroform, sover moontlik, afgedistilleer. Die donkergroen residu word omgekristalliseer uit petroleumeter (80°C. – 100°C.) na ontkleuring met dierkool. Die suurchloried word verkry as deurskynende, kleurlose plaatjies wat smelt by 84°C. – 85°C. Hoogstens sowat 40 persent van die difenielamien waarmee begin is, word uiteindelik verkry as die suurchloried. 'n Verskeidenheid van ongeidentifiseerde byprodukte word gevorm met die suurchloried.

Verestering met gesubstitueerde fenole

Uit die literatuur is drie metodes verkry waarvolgens die verestering bewerkstellig kan word, soos hier voorgestel:—



Metode I[4]

Volgens hierdie metode word ekwimolekulêre hoeveelhede van die difenielkarbamielchloried en die fenol saam verhit vir 2 – 3 uur onder 'n terugvloeikoeler. Na afloop van die reaksie word die gesmelte massa in verdunde swawelsuur gegooi, en na 'n dag of twee, kristalliseer die ester uit die olie wat gevorm is. Hoewel hierdie metode in sommige gevalle goeie resultate gee is dit tog nie as algemene metode geskik nie. In sommige gevalle is die kookpunt van die mengsel so hoog dat daar nie sprake is van kook onder 'n terugvloeikoeler nie en in sulke gevalle moet dit vir 'n lang tyd verhit word by 150°C. – 200°C. in 'n oliebad. Die reaksie is stadig. Opbreking van die stowwe vind ook plaas en die onsuiwerhede daardeur gevorm bemoeilik die kristallisering en suiwering van die gevormde ester.

Metode II[5]

Hierdie metode berus daarop dat die natriumsout (of waarskynlik enige metaalsout) van die fenol met 'n ekwimolekulêre hoeveelheid van die difenielkarbamielchloried, opgelos in alkohol, gekook word vir 'n paar uur onder 'n terugvloeikoeler. Die natriumchloried wat uitsak word affiltreer en die suurchloried word dan uitgekristalliseer.

Die natriumchloried lewer hier moeilikheid deurdat dit ook gedeeltelik in oplossing is en moeilik is om te skei van die ester. Verder is dit dikwels baie moeilik om die natriumfenolaat suiwer te berei.

Metode III[6]

Volgens hierdie metode word ekwivalente hoeveelhede van die suurchloried en die fenol met vier ekwivalente dele piridien verhit op 'n waterbad vir een uur. Daarna word die reaksiemengsel in water gegooi en 'n fyn kristallyne massa kristalliseer uit. Hierdie produk word gereinig deur dit om te kristalliseer uit petroleumeter (80°C. – 100°C.). Vir die doel van hierdie bereidings is dit gerieflik gevind om 'n groter oormaat piridien te gebruik en om die mengsel onder terugvloei te kook. Voordat die mengsel dan in water gegooi word, word die oormaat piridien afgestook onder verminderde druk.

Die 20 verbindings wat uitgetoets is was almal van die tipe $Ph_2NCOOAr$, en die volgende substituente was in -Ar teenwoordig in hierdie verbindings:—

(i) 4-chloro-(97°C.; 105·5°C. – 106·5°C.)[4];
(ii) 2-chloro-;
(iii) 2 : 4-dichloro-;
(iv) 2 : 4 : 6-trichloro-(143°C.; 154°C.)[4];
(v) 2 : 3 : 4 : 5 : 6-pentachloro-;
(vi) 2-metiel-(72°C. – 73°C.; 72·5°C. – 73·5°C.)[6];
(vii) 3-metiel-(100°C. – 101·2°C.; 99·5°C. – 101·5°C.)[6];
(viii) 4-metiel-(93°C. – 94°C.; 92·5°C. – 93·5°C.)[6];
(ix) 3-metiel-4-chloro-;
(x) 3-metiel-4-chloro-6-isopropiel-;

(xi) 2-nitro-(108°C. – 109°C.; 115°C. – 116°C.)[4];
(xii) 4-nitro-(112°C.; 118·5°C. – 119·5°C.)[4];
(xiii) Ar = feniel;
(xiv) 2 : 4 : 6-tribromo-;
(xv) 2-metiel-4 : 6-dibromo-;
(xvi) 2-metiel-4-nitro-;
(xvii) 2 : 6-dichloro-4-nitro-(132°C.; 140·5°C. – 141·5°C.)[4];
(xviii) Ar = β-naftiel (140·5°C. – 141·5°C.; 142°C. – 143°C.)[6];
(xix) 4-feniel.

Die di-feniel-karbamiel-chloried is ook uitgetoets en het toksies geblyk te wees teenoor termiete.

Die 2-metiel-4 : 6-nitro-feniel-difeniel-karbamaat is ook berei maar alleenlik in 'n onsuiwer toestand en is as sulks getoets en toksies gevind. Die stof is egter baie onstabiel teenoor lig en word baie vinnig bruin gekleur.

Die verskynsel is interessant en sal verder nagegaan word.

Die smeltpunte van sommige van die bogenoemde verbindings verskil aanmerklik van die soos deur vorige waarnemers gerapporteer. Hierdie temperature word in hakies genoem en wel in die volgorde: vorige waarnemer se smeltpunt; smeltpunt soos nou gevind.

Voorvermelde verbindings is almal volgens een van die drie metodes, wat hierbo genoem is, berei, en die wat in onderstaande tabel beskryf word is nie voorheen in die literatuur beskryf nie.

Nr.	*Metode van bereiding*	*Formule*	*Smeltpunt*	*Persent opbrengs*	*Samestelling*			
					Bereken		*Gevind*	
ii	I	$C_{19}H_{14}O_2NCl$	96·5°C. – 97·5°C.	36	70·47	4·36	70·23	4·43
iii	II	$C_{19}H_{13}O_2NCl_2$	111°C. – 112°C.	77	63·70	3·64	63·75	3·90
v	III	$C_{19}H_{10}O_2NCl_5$	202°C.	70	49·44	2·17	49·40	2·16
ix	III	$C_{29}H_{16}O_2NCl$	114·5°C. – 115°C.	55	71·08	4·78	71·06	4·38
x	III	$C_{23}H_{22}O_2NCl$	92·5°C. – 93·5°C.	—	72·71	5·84	72·76	5·81
xiv	III	$C_{19}H_{12}O_2NBr_3$	173·5°C. – 175°C.	52	43·37	2·30	43·27	1·90
xv	III	$C_{20}H_{15}O_2NBr_2$	139·5°C. – 140·5°C.	75	52·09	3·28	52·72	3·23
xvi	III	$C_{20}H_{16}O_4N_2$	131°C. – 132°C.	80	68·96	4·63	68·91	4·44

Toetse vir giftigheid

Die biologiese toetse is goedgunstiglik uitgevoer deur Mnr. B. K. Petty van die Afdeling Insektekunde, en aan hom is baie dank daarvoor verskuldig.

Die toetse is uitgevoer met die werkers van die termiet-spesie *Trinervitermes havilandii*. In die gevalle met die bestuiwings-poeiers is die insekte blootgestel in Petribakkies, op filtreerpapier wat bestuif is met die betrokke monster. Vyf persent DDT-poeier was ook ingesluit om 'n vergelyking te kan tref. Die insekte in aanraking met die DDT-poeier is gelaat vir 6 uur terwyl in die ander gevalle hulle gelaat is vir 4 uur en langer. Die termiete het vryelik aan die behandelde filtreerpapier gevreet en dus toon die syfers van mortaliteite beide die effekte van kontak—sowel as maagvergiftiging.

Hier volg die resultate van die toetse:—

Stof	*Vorm waarin getoets*	*Resultaat*
1. 4-chloro-feniel-difenielkarbamaat	20 persent in talkum	Geen toksisiteit
2. 2-chloro-feniel-difenielkarbamaat	do.	do.
3. 2 : 4-chloro-feniel-difenielkarbamaat	do.	do.
4. 2 : 4 : 6-trichloro-feniel-difenielkarbamaat ..	5 persent in talkum	do.
5. 2 : 3 : 4 : 5 : 6-penta-chloro-feniel-difenielkarbamaat	do.	do.
6. 2-metiel-feniel-difenielkarbamaat	do.	do.
7. 3-metiel-feniel-difenielkarbamaat	do.	Effens toksisiteit
8. 4-metiel-feniel-difenielkarbamaat	do.	Geen toksisiteit
9. 3-metiel-4-chloro-feniel-difenielkarbamaat ..	do.	do.
10. 3-metiel-4-chloro-6-isopropiel-feniel-difenielkarbamaat	do.	do.
11. 2-nitro-feniel-difenielkarbamaat	do.	10 persent toksisiteit na 36 uur
12. 4-nitro-feniel-difenielkarbamaat	do.	15 persent toksisiteit na 36 uur
13. Feniel-difenielkarbamaat	do.	8 persent toksisiteit na 36 uur
14. 2 : 4 : 6-tribromo-feniel-difenielkarbamaat ..	do.	3 persent toksisiteit na 36 uur
15. 2-metiel-4 : 6-dibromo-feniel-difenielkarbamaat ..	5 persent in talkum	Geen toksisiteit
16. 2-metiel-4-nitro-feniel-difenielkarbamaat	do.	1 persent toksisiteit na 36 uur
17. 2 : 6-dichloro-4-nitro-feniel-difenielkarbamaat ..	do.	3 persent toksisiteit na 96 uur
18. Ar = β-naftiel	do.	5 persent toksisiteit na 36 uur
19. 4-hidroksie-feniel-difenielkarbamaat	(Onsuiwer) in talkum	90 persent toksisiteit na 11 uur
20. 2-metiel-4 : 6-dinitro-feniel-difenielkarbamaat ..	(Onsuiwer) in talkum	80 persent toksisiteit na 36 uur
21. DDT	do.	100 persent toksisiteit na 24 uur
22. Difenielkarbamielchloried	do.	70 persent toksisiteit na 96 uur

Bostaande is sover as wat die reeks sinteses gevoer is. Hoewel daar geen uitstaande resultate verkry is wat betref toksisiteit van die esters nie, was die resultate tog so belowend dat 'n verdere volledige ondersoek van die trifeniel-karbamate helemal geregverdig is. Veral moet ingegaan word op die effekte van chloor- en nitro-substitusie in al drie feniel kerne.

Afdeling Skeikundige Diens,
Privaatsak,
Pretoria.

Ontvang 27 *Augustus*, 1949.

VERWYSINGS

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THE SYNTHESIS OF β-METHYL-PARACONIC ACID

by

H. A. CANDY and F. L. WARREN

OPSOMMING

Die sintese van β-metielparakonsuur (**XVI**) word beskryf. Hoë druk katalitiese reduksie van etiel-α-metiel-α-sianosuksinaat (**XI**) gee etiel-3-metiel-pirrolied-1-on-3-karboksilaat (**XIII**) wat deur gekonsentreerde soutsuur gehidroliseer na 3-*amino*-2-*metiel*-*propaan*-1 : 2-*dikarboksielsuurhidrochloried* (**XIV**), $C_6H_{12}O_4NCl$, smp. 196°C. Behandeling van die amiensuur met salpeterigsuur gee 2-*keto*-4-*metiel*-*tetrahidrofuraan*-4-*karboksilaat* (β-*metielparakonsuur*) $C_6H_8O_4$, smp. 79°C. – 80°C.

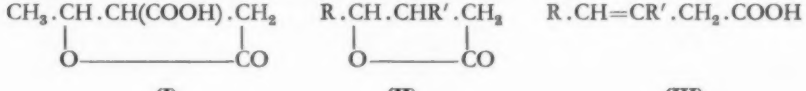
Pogings is aangewend om deur middel van ander kondensasies om hierdie suur uit etiel α-chloor-β-asetoksi-*iso*butiraat te verkry, sowel as van *asetoksi*-*asetoon*-*siaanhidrien* (**VII**) oor 1 : 2-*disiano*-2-*metiel*-3-*asetoksi*-*propaan*-.-*karboksilaat* (**IX**).

SUMMARY

The synthesis of β-methylparaconic acid (**XVI**) is described. High-pressure catalytic reduction of ethyl α-methyl-α-cyano-succinate (**XI**) gives ethyl 3-methyl-pyrrolid-1-one-3-carboxylate (**XIII**), which is hydrolysed by concentrated hydrochloric acid to 3-*amino*-2-*methyl*-*propane*-1 : 2-*dicarboxylic acid hydrochloride* (**XIV**), $C_6H_{12}O_4NCl$, m. p. 196°C. Treatment of this amino acid with nitrous acid gives 2-*keto*-4-*methyl*-*tetrahydrofuran*-4-*carboxylic acid* (β-*methylparaconic acid*), $C_6H_8O_4$, m. p. 79°C. – 80°C.

Other condensations to form this acid from ethyl α-chloro-β-acetoxy-*iso*butyrate (**VI**) as well as from *acetoxyacetone cyanhydrin* (**VII**) via 1 : 2-*dicyano*-2-*methyl*-3-*acetoxy*-*propane*-1-*carboxylate* (**IX**) were attempted.

In the degradation of naturally-occurring hydroxy-acids, there was obtained a product, $C_6H_8O_4$, which was a mono-carboxylic acid containing a lactone ring and which was difficult to esterify. The possibility of this being the unknown β-methylparaconic acid prompted the synthesis of this compound for comparison purposes. The paraconic acids are readily decomposed during distillation.

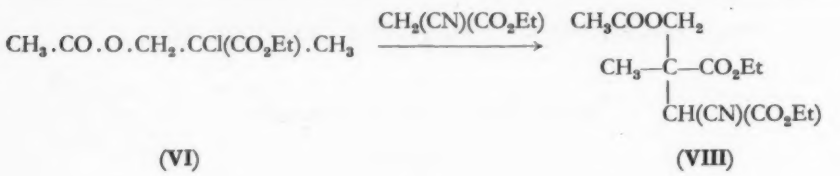


(**I**) (**II**) (**III**)

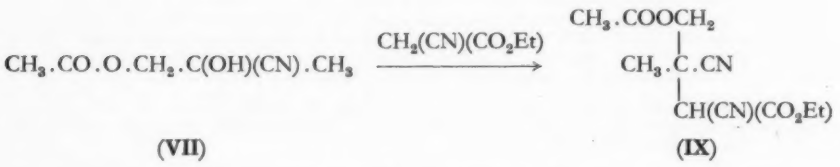
(**IV**) (**V**)

For example: γ-methylparaconic acid (**I**) under such treatment gives valerolactone (**II**; R=CH_3, R′=H) by decarboxylation, methylitaconic (**IV**) and methylcitraconic acids (**V**) by opening of the lactone ring, and β-pentenoic acid (**III**; R=CH_3, R′=H) by both these processes[1].

β-Methylparaconic acid (**XVI**) is of interest in that the presence of a β-methyl grouping should render the lactone ring more stable as the result of a Thorpe-Ingold valency deflection and preclude the formation of an unsaturated acid of types (**IV**) and (**V**). Any decomposition would have to be preceded by decarboxylation when the normal equilibrium of Linstead and Rydon[2] might operate to give the lactone (**II**; R=H, R′=CH_3) and the unsaturated acid (**III**; R=H, R′=CH_3). No decomposition products of the known α,α,β-trimethylparaconic acids are reported.



(VI) **(VIII)**

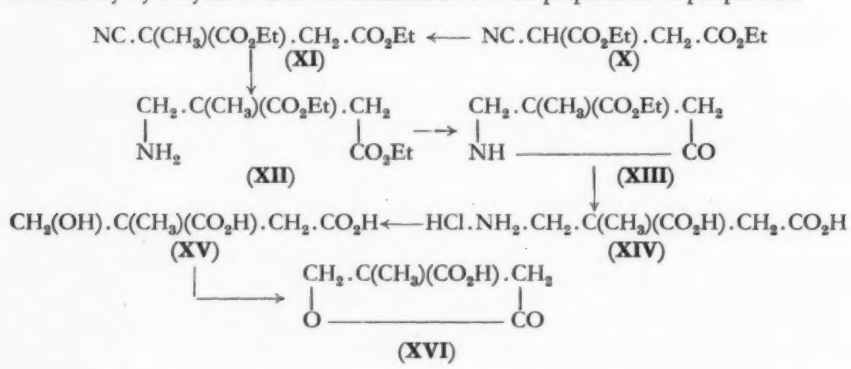


(VII) **(IX)**

The general methods employed for the preparation of α- and γ-alkylated paraconic acids are not readily applicable for the synthesis of the β-substituted acids. Attempts to synthesize the acid with the hydroxyl group in place *via* compounds (**VIII**) and (**IX**) necessiated a malonic ester condensation with a tertiary halogen compound. Auwers and Fritzweiler[3] report that ethyl α-bromo*iso*butyrate condensed with ethyl sodiomalonate only at elevated temperatures under pressure, and then the required reaction was accompanied by loss of hydrobromic acid followed by a Michael condensation to give α-methylglutaric acid. Henstock and Sprankling[4] record the formation of ethoxy acids. On the other hand, with cyanacetic ester and xylol as solvent, Bone[5] reported good yields of succinic acids. However, attempts to condense ethyl α-chloro-β-acetoxy*iso*-butyrate (**VI**), prepared by the method of Fourneau and Tiffeneau[6], with cyanacetic ester in xylol, to obtain (**VIII**) were unsatisfactory.

The formation of succinic acids by the condensation of cyanhydrins with ethyl sodiocyanacetate outlined by Higson and Thorpe[7] was attempted with acetoxyacetone cyanhydrin (**VII**). A small yield of oil was obtained corresponding to *ethyl* 1 : 2-*dicyano*-2-*methyl*-3-*acetoxy*-*propane*-1-*carboxylate*, $C_{11}H_{14}O_4N_2$ (**IX**). Hydrolysis, however, failed to give any β-methylparaconic acid.

The synthesis of β-methylparaconic acid was finally effected by the method employed successfully by Polyakova and Preobrazhenski[8] for the preparation of pilopic acid.



(XI) **(X)** **(XII)** **(XIII)** **(XV)** **(XIV)** **(XVI)**

The ethyl α-methyl-α-cyanosuccinate (**XI**) was prepared by the condensation of ethyl cyanoacetate with ethyl chloracetate to give a mixture of ethyl cyanosuccinate and triethyl β-cyanotricarballylate which were readily separated by distillation. The ethyl cyanosuccinate was then condensed with methyl iodide to give ethyl α-methyl-α-cyanosuccinate (**XI**). The alternative route *via* the ethyl α-cyanopropionate was not employed in view of the difficulty of separating this from the α-cyano*iso*butyrate formed in the same reaction. The method of Zelenski and Bitschicken[9] for the formation of ethyl cyanosuccinate directly from ethyl chloracetate gave larger quantities of ethyl carballylate.

The ethyl methylcyanosuccinate (**XI**) was catalytically hydrogenated under pressure under different conditions. An oil was always obtained in small yield whilst ammonia was always present as one of the reduction products indicative of the formation of a secondary amine. The oil which failed to give nitrogen with nitrous acid was almost certainly the ethyl 3-methyl-pyrrolid-1-one-3-carboxylate (**XIII**) formed by ring closure of the primary reduction product ethyl α-methyl-α-aminomethylsuccinate (**XII**). Boiling the pyrrolidone (**XIII**) with barium hydroxide failed to open the ring to a primary amine or to hydrolyse the ester group, although this method was successfully used by Polyakova and Preobrazhenski[8] to hydrolyse their pyrrolidone.

The failure to hydrolyse the ester is certainly due to the tertiary nature of this carbethoxyl group, whilst the presence of two carbon groupings on the β-carbon atom causes a Thorpe-Ingold valency deflection and stabilizes the pyrrolidone ring. Hydrolysis was finally effect by boiling with strong hydrochloric acid to give 3-*amino*-2-*methyl-propane*-1 : 2-*dicarboxylic acid hydrochloride* (**XIV**), $C_6H_{12}O_4NCl$, m. p. 196°C. Treatment of this acid with nitrous acid gave a copious evolution of nitrogen to yield the hydroxy acid (**XV**) which immediately ring-closed to 2-*keto*-4-*methyl-tetrahydrofuran*-4-*carboxylic acid* (*β-methylparaconic acid*) (**XVI**), $C_6H_8O_4$, m. p. 79°C. – 80°C. The acid was characterized further by the preparation of the p-*phenylphenacyl ester*, m. p. 117°C. – 118°C.

In view of the small yield it was not possible to study further the reactions of the acid.

EXPERIMENTAL

1. Ethyl α-chloro-β-acetoxy-isobutyrate (VI)

This was prepared by the method of Fourneau and Tiffeneau[6] and obtained as a colourless oil, b. p. 114°C. – 120°C./25 mm. (Fourneau and Tiffeneau give b. p. 216°C. – 217°C./760 mm.)

Analysis

Found: Cl, 16·9. $C_8H_{13}OCl$
requires Cl, 17·0%.

2. Acetoxyacetone cyanhydrin (VII)

Acetoxyacetone (98 g.; 1 mol.) prepared by the method of Kling[10] was treated with liquid HCN (28 g.; 1·2 mols.) in the presence of K_2CO_3 (0·5 g.) at 10°C. and allowed to warm up to room temperature. Concentrated sulphuric acid (5 drops) was then added and the product distilled under reduced pressure. Redistillation gave *acetoxyacetone cyanhydrin* as a colourless liquid, b. p. 142°C. – 143°C./25 mm. Yield 72 grams; 60 per cent.

Analysis

Found: N, 9·9. $C_6H_9O_3N$
requires N, 9·8%.

3. Ethyl 1 : 2-dicyano-2-methyl-3-acetoxy-propane-1-carboxylate (IX)

Ethyl cyanoacetate (37·8 g.; 0·9 mol.) was added to sodium ethoxide made by dissolving sodium (7·7 g.; 0·9 mol.) in anhydrous ethanol (86·8 g.; 5 mols.). The sodio derivative was then added slowly to acetoxyacetone cyanhydrin (47·8 g.; 1 mol.) cooled in ice. After standing for two hours at room temperature during which the solution darkened slightly, a large excess of water was added and then made slightly acid with concentrated hydrochloric acid. The oil which separated was extracted with ether. The ethereal solution, washed with water and dried over calcium chloride, gave a thick brown oil giving two fractions (i) b. p. 60°C. – 120°C./1 mm. and (ii) b. p. 120°C. – 200°C./1 mm. Considerable polymerization occurred during distillation. Redistillation of fraction (ii) gave a product, b. p. 190°C./1 mm. Yield 5·6 per cent.

Analysis

Found: N, 11·4. $C_{11}H_{14}O_4N_2$
requires N, 11·7%.

4. Ethyl α-methyl-α-cyanosuccinate (XI)

Methyl iodide (28·5 g.; 1 mol.) was added slowly to the sodium derivative of ethyl cyanosuccinate (40 g.; 1 mol.) in absolute alcohol and refluxed for 2 hours. The solvent was removed under reduced pressure, water added, and the oil separated and dried by azeotropic distillation with benzene. The ethyl α-methyl-α-cyanosuccinate distilled at 160°C./15 mm. Yield 70 per cent. Barthe[11] gives b. p. 189°C. – 190°C./80 mm. Hydrolysis of a sample gave methylsuccinic acid, m. p. 108°C. – 110°C. Bone and Sprankling[12] give m. p. 111°C.

5. α-Methyl-α-aminomethyl-succinic acid hydrochloride (XIV)

Ethyl α-methyl-α-cyanosuccinate (12 g.) in glacial acetic acid (60 g.) and concentrated sulphuric acid (6 g.) was hydrogenated under pressure in the presence of palladium-platinum oxide on charcoal. The initial pressure of 26 kg./cm.² fell slowly during seven hours to 8 kg./cm.².

Volume of gas space = 140 c.c.
Volume of H_2 at 26 kg./cm.² = 3·52 litres
Volume of H_2 at 8 kg./cm.² = 1·08 litres
H_2 consumed = 2·44 litres
Calc. for 2 mols. of $C_9H_{15}O_4N$, H_2 = 2·67 litres.

Similar reductions were carried out without improvement of yield but at different rates under the following conditions:—

Reagents	*Catalyst*	*Initial pressure kg./cm²*	*Time required hours*
As above	As above	60	3
As above	PtO_2	52	5½
Abs. ethanol saturated with NH_3	Raney Ni	57	15

The solution was filtered and distilled under reduced pressure leaving an oily mass of crystals. Water was added and the solution extracted with ether. The ether solution gave an oil (ca. 2 g.) which was shown to be unchanged ester by hydrolysis to methyl-succinic acid, m. p. 109°C. The aqueous solution was treated with barium carbonate to remove sulphuric acid, filtered and the filtrate evaporated on a water bath to give a clear viscous liquid, which gave no reaction with nitrous acid, and which was almost certainly ethyl-3-methyl-pyrrolid-1-one-3-carboxylate (**XIII**). The liquid was refluxed with concentrated hydrochloric acid (50 c.c. of 1 : 1) for 2 hours. The oily, colourless crystals, obtained by evaporation, were dissolved in a minimum of water, cooled to 0°C. and saturated with hydrochloric acid gas which precipitated a crystalline mass. Recrystallization by the same procedure gave 1·5 grams of 3-*amino*-2-*methyl-propane*-1 : 2-*dicarboxylic acid hydrochloride* as colourless prisms, m. p. 196°C.

Analysis

Found: C, 36·35; H, 6·1; Cl, 18·1; N, 7·0. $C_6H_{12}O_4NCl$
requires C, 36·5; H, 6·1; Cl, 18·0; N, 7·1 %.

6. β-Methylparaconic acid

A solution of α-methyl-α-aminomethyl-succinic acid hydrochloride (0·7 g.; 1 mol.) in water (3 g.) was cooled to 0°C. and a cold concentrated solution of sodium nitrite (0·25 g.; 1 mol.) added in two portions when a copious evolution of nitrogen was observed. After 4 hours at 0°C. and then 15 hours at room temperature, the solution was warmed to 40°C. for one hour. The solution was extracted with ether and the ethereal extract gave a colourless oil which partially crystallized on standing. A further yield of oil was obtained by evaporating the aqueous solution to dryness and extracting with ether. The crystals were soluble in ether, methanol, ethanol and water and insoluble in chloroform, carbon tetrachloride and light petroleum. The substance sublimed at 70°C./0·01 mm. but the sublimate was not free from oil. Crystallization from pure dry benzene gave 2-*keto*-4-*methyl-tetrahydrofuran*-4-*carboxylic acid*, m. p. 79°C. – 80°C.

Analysis

Found: Eq. wt. 144·0. $C_6H_8O_4$
requires Eq. wt. 144·1.
Found: C, 50·4; H, 5·5. $C_6H_8O_4$
requires C, 50·0; H, 5·6%.

7. *p*-phenylphenacyl ester of β-methylparaconic acid

p-Phenylphenacyl ester of β-methylparaconic acid crystallized from alcohol in pearly plates, m. p. 117°C. – 118°C.

Analysis

Found: C, 70·8; H, 5·6. $C_{20}H_{18}O_5$
requires C, 71·0; H, 5·4%.

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A THEORETICAL INVESTIGATION OF SOME PROPERTIES OF LIQUIDS

PART II. ON THE SIZE OF HOLES IN LIQUIDS

by

H. A. E. MACKENZIE

OPSOMMING

Die inkremente in die termodinamiese potensiaal van aktivering vir die verdamping en viskeuse stroming van 'n vloeistof word op so 'n wyse bereken dat, deur hulle te vergelyking met gewone termodinamiese hoeveelhede, resultate van fisiese belang aantoon. Hulle staan in verband met die termodinamiese potensiaal aan die oppervlakte in terme van 'n parameter wat die grootte van die gate in die vloeistof aandui. Hierdie parameter word verskeie vloeistowwe bereken en in alle gevalle dui die waarde van die parameter aan dat die gate van molekulêre grootte is. Daar word op attent gemaak dat die argumente wat hier aangevoer word nie van toepassing is in die geval van vloeistowwe waar van die molekule aansienlik van sferiese simmetrie afwyk nie.

SUMMARY

The thermodynamic potential increments of activation for the evaporation and viscous flow of a liquid are calculated in such a way that their comparison with ordinary thermodynamic quantities will be physically significant. They are related to the surface thermodynamic potential in terms of a parameter which is a measure of the size of the holes in the liquid. This parameter is evaluated for several liquids and in all cases its value indicates that the holes are of molecular size. It is pointed out that the arguments used here are inapplicable in the case of a liquid whose molecules deviate considerably from spherical symmetry.

The molar thermodynamic potential increment of activation for viscous flow, $\triangle G^*_{vis}$, has been defined[1] by

$$\eta = h.v^{-1}.\exp(\triangle G^*_{vis}/RT), \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where η is the viscosity of the liquid, v is the volume occupied by one molecule in the liquid, h and R have their conventional meanings and T is the absolute temperature. Powell, Roseveare and Eyring[2] have shown that, for a large number of liquids,

$$\triangle G^*_{vis} = \triangle E_{vap}/2{\cdot}45, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where $\triangle E_{vap}$ is the energy of vaporization of the liquid.

By applying the theory of rate processes to evaporation, using a smoothed potential model for a liquid, the author[3] has calculated the energy of activation for viscous flow in terms of the energy of vaporization and obtained a similar result. Brunner[4] has recently pointed out, however, that $\triangle G^*_{vis}$ defined by equation (1) involves the conventional frequency factor, kT/h, of the transition state theory, so that comparisons between $\triangle G^*_{vis}$ and ordinary thermodynamic quantities such as the energy of vaporization, while they may be useful, do not have any real physical meaning.

In Eyring's treatment of the thermodynamics of the transition state,[5] the specific rate of a process is

$$j = (kT/2\pi m^*)^{\frac{1}{2}}.K_c^*/\delta, \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where m* is the effective mass of the activated complex, δ is the length of the pass over the barrier in the potential energy surface, and

$$K_c^* = F^*/F, \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where F^* is the complete partition function of the activated complex and F is that of the initial state. F^* is written as

$$F^* = f^*_{trans}.(F^*)', \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and a new equilibrium constant, K*, is defined by

$$K^* = (F^*)'/F = K_c^*/f^*_{trans}, \quad \ldots\ldots(6)$$

where f^*_{trans}, the translational partition function of the activated complex in the co-ordinate of reaction, is given by

$$f^*_{trans} = (2\pi m^* kT)^{\frac{1}{2}} . h^{-1} . \delta. \quad \ldots\ldots(7)$$

Equations (3), (6) and (7) together give

$$j = (kT/h) . K^*. \quad \ldots\ldots(8)$$

The general relation,

$$\triangle G^\circ = -RT . \ln K, \quad \ldots\ldots(9)$$

gives, with equation (3),

$$j = (1/\delta) (kT/2\pi m^*)^{\frac{1}{2}} . \exp(-\triangle G_c^*/RT), \quad \ldots\ldots(10)$$

and, with equation (8),

$$j = (kT/h) . \exp(-\triangle G^*/RT), \quad \ldots\ldots(11)$$

where the $\triangle G$ are understood to refer to standard state conditions. Brunner (*loc. cit.*) suggests that the quantity $\triangle G_c^*$ should be used for comparisons with ordinary thermodynamic quantities rather than $\triangle G^*$, and has applied this suggestion with some success to the derivation of an expression for viscosity in terms of energy of vaporization.

Following Brunner's suggestion, we obtained for the viscosity of a liquid

$$\eta = (\delta_{vis}/\kappa_{vis}) (2\pi mkT)^{\frac{1}{2}} . v^{-1} . \exp\{(\triangle G_c^*)_{vis}/RT\}, \quad \ldots\ldots(12)$$

where m* has been replaced by m, the mass of one molecule of the liquid and the transmission coefficient, κ_{vis}, is included for generality. The specific rate of vaporization of the liquid, j_e, is given by

$$j_e = (\kappa_{vap}/\delta_{vap}) (kT/2\pi m)^{\frac{1}{2}} . \exp\{-(\triangle G_c^*)_{vap}/RT\}, \quad \ldots\ldots(13)$$

where κ_{vap} is the transmission coefficient for evaporation. The Herz-Knudsen equation gives[6]

$$j_e = a(m/2\pi kT)^{\frac{1}{2}} . v^{-\frac{1}{3}} . p/d, \quad \ldots\ldots(14)$$

where p is the vapour pressure of the liquid, d its density and a is the accommodation coefficient. By eliminating j_e between equations (13) and (14) we obtain

$$(d/p) = (a . \delta_{vap}/\kappa_{vap}) (m/kTv^{\frac{1}{3}}) . \exp\{(\triangle G_c^*)_{vap}/RT\}. \quad \ldots\ldots(15)$$

The precise meaning of the parameter δ in processes such as evaporation and viscous flow is obscure; we may not, for example, evaluate δ_{vis} or δ_{vap} with the aid of a potential energy diagram. It seems reasonable, however, since δ has the dimensions of length, to assume a linear dependence of δ on $v^{\frac{1}{3}}$ and write

$$\delta_{vis} = x . v^{\frac{1}{3}}, \quad \ldots\ldots(16)$$

$$\text{and} \quad \delta_{vap} = x' . v^{\frac{1}{3}}, \quad \ldots\ldots(17)$$

where x and x′ are temperature independent constants.
Substituting these values for the δ in equations (12) and (15) we obtain, by taking logarithms after a slight rearrangement:

$$\log(\eta/d^{\frac{2}{3}}T^{\frac{1}{2}}) = \{(\triangle G_c^*)_{vis}/2{\cdot}303RT\} + \log\{x(2\pi k)^{\frac{1}{2}}/\kappa_{vis}.m^{\frac{1}{6}}\}, \quad \ldots.(18)$$

and $$\log(dT/p) = \{(\triangle G_c^*)_{vap}/2{\cdot}303RT\} + \log\{x'.ma/k.\kappa_{vap}\}. \quad \ldots\ldots(19)$$

The plots of $\log(\eta/d^{\frac{2}{3}}T^{\frac{1}{2}})$ and $\log(dT/p)$ against $1/T$ are in general not linear for a liquid, but very nearly so. The deviation from linearity may be due to the functional dependence of $(\triangle G_c^*)_{vis}$ or κ_{vis} and of $(\triangle G_c^*)_{vap}$ or (a/κ_{vap}) on temperature, but, in order to facilitate the application of equations (18) and (19), it will be assumed here that a and the κ are independent of temperature. Differentiation of (18) and (19) then yields:

$$(\triangle G_c^*)_{vis} = 2{\cdot}303\ R\left\{d\log(\eta/d^{\frac{2}{3}}T^{\frac{1}{2}})\right\}/d(1/T) \quad \ldots\ldots\ldots(20)$$

and $$(\triangle G_c^*)_{vap} = 2{\cdot}303\ R\left\{d\log(dT/p)\right\}/d(1/T). \quad \ldots\ldots\ldots\ldots(21)$$

For a small temperature range from T_1 to T_2, over which the $(\triangle G_c^*)$ may be regarded as constant, we have

$$(\triangle G_c^*)_{vis} = \frac{2{\cdot}303\ R.T_1.T_2}{(T_2-T_1)}\ \log\left(\frac{\eta_1.d_2^{\frac{2}{3}}.T_2^{\frac{1}{2}}}{\eta_2.d_1^{\frac{2}{3}}.T_1^{\frac{1}{2}}}\right) \quad \ldots\ldots\ldots(22)$$

and $$(\triangle G_c^*)_{vap} = \frac{2{\cdot}303\ R.T_1.T_2}{(T_2-T_1)}\ \log\left(\frac{d_1.T_1.p_2}{d_2.T_2.p_1}\right), \quad \ldots\ldots\ldots\ldots(23)$$

where the numerical suffixes on the d, p and η indicate at which temperature the quantities are determined. These expressions provide a means for the calculation of the thermodynamic potential increments of activation for viscous flow and evaporation which are physically comparable with ordinary thermodynamic quantities.

We shall be concerned, in particular, with the relationship between $(\triangle G_c^*)_{vis}$, $(\triangle G_c^*)_{vap}$ and the surface thermodynamic potential of a liquid. By regarding a liquid as a system of close-packed spheres, Telang[7] has calculated $\triangle G_s$, the thermodynamic potential increment associated with the formation of sufficient fresh surface to accommodate 1 mole of liquid in the surface. He obtains the result:

$$\triangle G_s = 1{\cdot}091\ N^{\frac{1}{3}}.\gamma.(M/d)^{\frac{2}{3}}, \quad \ldots\ldots\ldots\ldots\ldots(24)$$

where γ is the surface tension of the liquid. The numerical factor arises from geometrical considerations based on the assumption of close packing.

If we make no assumptions about the packing of spheres, but regard the molecular volume, v, as a small cube of side $v^{\frac{1}{3}}$, we obtain (24) without the numerical factor and by a much shorter argument, for in each cm.^{2} of surface there will be $v^{-2/3}$ molecules so that the surface thermodynamic potential per molecule will be

$$\gamma.v^{\frac{2}{3}}, \text{ giving } \triangle G_s = N.\gamma.v^{\frac{2}{3}} = N^{\frac{1}{3}}.\gamma.(M/d)^{\frac{2}{3}}. \quad \ldots\ldots\ldots(25)$$

It seems that nothing is to be gained by using (24) in preference to (25) and, in fact, the simpler concept is more useful in the discussion which follows.

Telang (*loc. cit.*) adopts a somewhat novel interpretation of the processes involved in viscous flow. Whereas Eyring and his collaborators have regarded activation for viscous flow as a dual process involving, firstly, the formation of a hole in the liquid and, secondly, the movement of a molecule into a hole, Telang regards it as being

identical with the transfer of a molecule from the interior of a liquid into its surface. In order to avoid confusion, we shall state our interpretation of the process here, since it is rather different from either of those which we have cited.

We shall assume, with Eyring and others, that the process of fusion is attended by the introduction of a large number of holes into the system. The essential process in the viscous flow of a liquid will then be regarded as the movement of a molecule from the surface of a hole into the hole itself. $(\triangle G_c^*)_{vis}/N$ will thus represent the thermodynamic potential increment accompanying the transfer of one molecule from the surface of a hole to the transition state for viscous flow. The thermodynamic potential increase associated with the formation of a hole will be $\beta . \triangle G_s/N$, where β is the number of molecules bordering on a hole. β is thus a measure of the size of the hole; a hole of molecular size, which we shall regard as a small cube of volume v, would, for example, have six molecules bordering it. It is clear then that the transfer of one molecule of a liquid from the bulk of the liquid (*i.e.*, not from the surface of a hole) to the transition state for viscous flow will require a thermodynamic potential of $\{(\triangle G_c^*)_{vis} + \beta . \triangle G_s\}/N$, since such a process will entail both the creation of a hole and the subsequent movement into the hole.

Similarly it may be argued that the transfer of one molecule of a liquid from the body of the liquid to the transition state for evaporation will require a thermodynamic potential of $\{(\triangle G_c^*)_{vap} + \triangle G_s\}/N$. If now we assume that the transition states for evaporation and viscous flow are identical, it follows that

$$(\triangle G_c^*)_{vis} + \beta . \triangle G_s = (\triangle G_c^*)_{vap} + \triangle G_s. \quad \ldots\ldots\ldots\ldots (26)$$

β may readily be determined by calculation, since, from equation (26),

$$\beta = \{(\triangle G_c^*)_{vap} - (\triangle G_c^*)_{vis}\}/\triangle G_s + 1. \quad \ldots\ldots\ldots\ldots (27)$$

The calculation has been carried through for a number of liquids and the results are given in the table. The equations used in the calculations are (22), (23), (25) and (27). Experimental data have been obtained from tables of physical constants[8].

For the non-associated liquids and water β has a value of 6 approximately, suggesting that the holes in these liquids are equal in size to the molecular volume. The similarity in behaviour of the non-associated liquids and water suggests that association in the latter is of such a character that it does not give rise to stable polymers of H_2O. This is in accord with other experience. On the other hand, it is well established[9] that liquid acetic acid consists of dimeric molecules. This correlates with the fact that β for acetic acid is approximately 6 if the molecule is taken to be the dimer, whereas, if monomeric acetic acid is assumed, β has a value of 9·5.

High values of β in the case of methyl and ethyl alcohols would point to the formation of definite polymers, akin to the acetic acid dimer, in addition to the dynamic type of association found in the case of water.

It should be mentioned here that the liquids included in the table are, very approximately, spherical in shape. The simple treatment used will not be applicable in the case of long chain molecules and the somewhat large value for β in the case of ethyl acetate may be due to deviation from spherical symmetry.

It may be concluded, however, in the absence of conflicting evidence, that the holes in a liquid are equal in size to the molecular volume; but that, where stable polymers exist in the liquid, the size of the holes is equal to the volume of the polymeric molecule.

Liquid	*M*	*T* °K.	η (*cps.*)	*d* (*g. ml*$^{-1}$)	*p* (*mm.*)	γ (*dyne-cm*$^{-1}$)	*Mean* $(\triangle G_c^*)_{vis}$ (*k cal.*)	*Mean* $(\triangle G_c^*)_{vap}$ (*k cal.*)	$\triangle G_f$ (*k cal.*)	β
Carbon tetrachloride		293·2	0·969	1·595	91·0	—	2·62	7·51	—	—
		313·2	0·739	1·555	215·8	—			—	—
	153·8	303·2	—	1·575	—	24·7	—	—	1·06	5·6
Chloroform		293·2	0·568	1·490	160·5	—	1·92	6·75	—	—
		313·2	0·467	1·449	369·3	—			—	—
	119·4	303·2	—	1·468	—	25·5	—	—	0·966	6·0
Benzene		293·2	0·652	0·8788	74·13	—	2·52	7·73	—	—
		313·2	0·503	0·8573	180·2	—			—	—
	78·11	303·2	—	0·8680	—	27·6	—	—	1·12	5·7
Water		283·2	1·308	0·9997	9·209	—	4·45	10·0	—	—
		303·2	0·8007	0·9957	31·82	—			—	—
	18·02	293·2	—	0·9982	—	72·75	—	—	1·01	6·5
Acetic acid		293·2	1·232	1·049	11·2	—	3·18	10·1	—	—
		303·2	1·040	1·039	20·3	—			—	—
(Dimer)	120·1	298·2	—	1·044	—	27·0	—	—	1·29	6·4
(Monomer)	60·05	298·2	—	1·044	—	27·0	—	—	0·812	9·5
Ethyl acetate		283·2	0·512	0·9109	42·8	—	2·26	8·34	—	—
		303·2	0·400	0·8882	118·7	—			—	—
	88·10	293·2	—	0·8992	—	22·55	—	—	0·968	7·3
Methyl alcohol		293·2	0·597	0·7915	96·0	—	2·62	8·71	—	—
		313·2	0·456	0·7740	260·5	—			—	—
	32·04	303·2	—	0·7825	—	21·9	—	—	0·525	12·6
Ethyl alcohol		293·2	1·200	0·7895	44·00	—	3·48	9·72	—	—
		313·2	0·834	0·7722	133·4	—			—	—
	46·07	303·2	—	0·7810	—	21·1	—	—	0·645	10·7

Following Eyring[1] we have regarded the "holes" in a liquid as vacant sites rather than as "more or less widened gaps between the molecules". Criticism of this approach by Frenkel[10] does not seem sufficiently well-founded to discredit Eyring's very useful calculations. In particular the present work tends to support the idea that the "holes" in liquids may be treated as vacant sites; at least, that is, the "holes" involved in the mechanism of viscous flow.

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THE KINETICS OF THE UNCATALYSED DEHYDRATION OF OXALIC ACID IN ACETIC ACID-ACETIC ANHYDRIDE MIXTURES

by

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OPSOMMING

Die dehidrasie van oksaalsuur in mengsels van asynsuur en asynsuuranhidried is bestudeer met behulp van volumetriese meting van die vrygesette gasse in 'n spesiaal ontwerpte gasburet. Die reaksie is eenvoudig en kan verklaar word as deel van 'n bimolekulêre proses waarin oksaalsuur en asynsuuranhidried molekule betrokke is. Reaksiesnelheid vergelykings by 30°C. en die energie van aktivering is bepaal. Hieruit kan die frekwensie faktor en die entropie van aktivering bereken word.

Die meganisme van die reaksie is volgens die beginsels van die botsingsteorie en van die oorgangstadiumteorie beskou. Laasgenoemde bied 'n eenvoudiger verklaring van die feite. Die makroskopiese viskositeit van die reaksiemengsel het nie 'n noemenswaardige uitwerking op die reaksiesnelheid nie. Katalise deur kaliumasetaat ('n sterk base in hierdie medium) en deur mineraalsure word vermeld.

SUMMARY

The dehydration of oxalic acid in acetic acid-acetic anhydride mixtures has been studied by volumetric measurement of the evolved gaseous products in a specially designed gas burette. The reaction is simple and may be interpreted on the basis of a bimolecular process involving oxalic acid and acetic anhydride molecules. Rate equations at 30°C. and the energy of activation for the reaction have been determined. Hence the frequency factor and the entropy of activation are calculated.

The mechanism of the reaction has been considered on the basis of the collision theory and the transition state theory. The latter affords a more simple explanation of the facts. The macroscopic viscosity of the reaction mixture has been shown to have no significant effect on the reaction rate. Catalysis by potassium acetate (a strong base in this medium) and by mineral acid are reported.

INTRODUCTION

Although the decompositions of formic acid[1] and of oxalic acid[2] in concentrated sulphuric acid have been investigated kinetically, there is little information on the dehydration of aliphatic acids in acetic acid-acetic anhydride mixtures. Schierz[3] has studied the decomposition of formic acid in acetic anhydride, a reaction which is markedly catalysed by mineral acids and tertiary nitrogen bases. He mentions that a kinetic study of the dehydration of oxalic acid by a gasometric method is rendered difficult by the appreciable solubility of carbon dioxide. England and Mackenzie[4], however, have shown that such a difficulty is easily surmounted.

Mackenzie and Winter[5] have recently reviewed the properties of the system acetic acid-acetic anhydride and shown that it behaves as an ideal mixture for concentrations of acetic anhydride up to 80 per cent w/w provided that acetic acid is regarded as dimeric. They have proposed that acetyl ions exist in this solvo-system in concentration determined by the equilibrium

$$AcOH_2^+ + Ac_2O = Ac^+ + (AcOH)_2.$$

Since there is as yet no direct method for studying this reaction, the present work was undertaken in the hope of obtaining further circumstantial evidence for its existence. This paper deals mainly with work on the uncatalysed dehydration of oxalic acid which is a necessary preliminary to the study of the catalysed reaction.

The preparation of materials

Pure anhydrous oxalic acid was prepared by a method based on the work of Johnson and Partington[6]. Successive portions of toluene were distilled from a sample of "Analar" hydrated oxalic acid until the distillate was obtained water-free. The residual mixture of oxalic acid and toluene was cooled and the anhydrous oxalic acid filtered

off. The crystals were washed with a little dry benzene, dried by stirring rapidly in air, ground up and stored over phosphorus pentoxide[7] and paraffin wax (to absorb the benzene) in a vacuum desiccator. Six volumetric determinations of the final product with sodium hydroxide solution, previously standardized against potassium hydrogen phthallate, gave a mean analysis of 100·2 per cent $(COOH)_2$.

The acetic acid was purified by the method of Hutchison and Chandlee[8], entailing a ten-hour treatment of the boiling acid with an excess of chromic oxide followed by fractional distillation in a column similar to that of Marshall[9] and using a reflux ratio 8. The final product had $n_D^{20} = 1{\cdot}37193$ which may be compared with the value given by Heilbron[10], $n_D^{20} = 1{\cdot}37182$. The most recent determination, that by Vogel[11], gives $n_D^{20} = 1{\cdot}37151$. Vogel's method of purification, however, does not appear to be as good as that of Hutchison and Chandlee, whose product (m.p. 16·55°C.) was comparable in purity to that obtained by Kolthoff[12] by fractional crystallization (m.p. 16·62°C.).

The acetic anhydride was purified by fractional distillation in the column used for acetic acid. The product was collected over a range less than 0·5°C. and had $n_D^{20} = 1{\cdot}39064$, which may be compared with the accepted value[10] of $n_D^{20} = 1{\cdot}39038$.

Method of following the reaction

The reaction was followed by volumetric measurement of the evolved gases at constant pressure. Previous workers have shown that in such rate determinations the liquid must be well stirred or shaken and that there should be little or no unthermostated gas space[13]. The apparatus, therefore, was designed so that the products could be collected below the water level in a thermostat, while measurements were taken above.

A diagram of the apparatus is given in Fig. 1. It consists mainly of three burettes. The reaction vessel, A, is connected to the burette, B, which in turn is joined to another burette, C, by 4 mm. glass tubing, as shown. B and C have precisely the same bore, and this is achieved by using two halves of the same burette for these components. The length from B to C is somewhat greater than the local barometric height. The tap t_1 leads to a vacuum pump. From the tube joining B and C a lead is taken to D, the other burette, and the lead may be closed by the capillary tap, t_2. The tap, t_3, connects D to a water pump. By evacuating C and D the apparatus is filled with mercury, so that when the level in D is at 1_D, a graduated mark, the levels in B and C are at 1_B and 1_C respectively.

If B is opened to the atmosphere, t_2 opened and 1 ml. withdrawn into D, the levels in B and C will each fall by an amount equivalent to 0·5 ml. If this is done with B closed, the level in B will fall less than the level in C.

The reaction vessel A is so designed that the reactants do not mix until shaking is started. It is attached to B with a length of pressure tubing and the level in D is adjusted to 1_D while A is still open to the air. A solution of oxalic acid in acetic acid is introduced into one compartment of A and acetic anhydride is placed in the other. The level at 1_C is noted, A closed and the reaction started by shaking the reaction vessel with the aid of a motor-driven cam. Shaking is continued throughout the run. 1 ml. of mercury is withdrawn into D and the levels fall to 2_B and 2_C respectively. The distance $1_C - 2_C$ is greater than $1_B - 2_B$. As gas is evolved from the reaction mixture the level in B falls while that in C rises until, when the pressure inside the reaction vessel is again at its initial value, 2_C is just 0·5 ml. below 1_C. At this stage exactly 0·5 ml. of gas has been evolved and the time is noted.

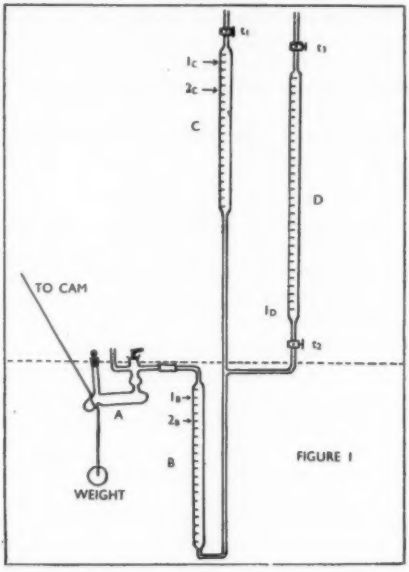


FIGURE 1

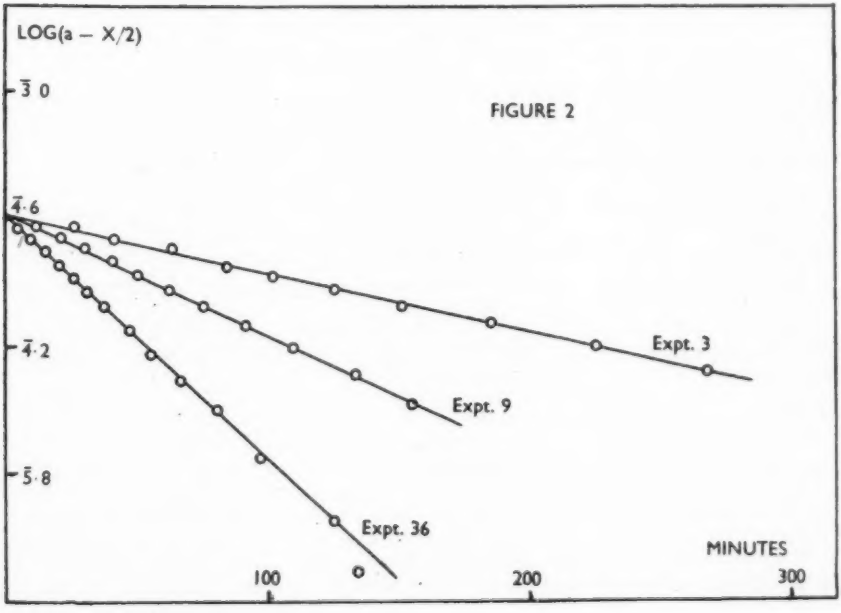


FIGURE 2

The process is repeated again and again during the course of the reaction. At the end of a run A and D are opened and the level in D is restored to 1_D. As the diagram shows, the gas was collected entirely below the level of the thermostat bath. The temperature of the latter was maintained constant during a particular run to within 0·02°C.

The measurement of volumes is thus reduced to the observation of small pressure changes, resulting in greater accuracy.

Correction factors

The interpretation of the results is complicated by two factors. The first, of course, is the vapour pressure of the solvent mixture. This was obtained by interpolation, making use of the known ideality of acetic acid-acetic anhydride mixtures[5] and ignoring the small effect of the solute. Since vapour pressure data at temperatures near room temperature were not available, these were obtained for pure acetic acid and pure acetic anhydride by linear extrapolation of the curve $\log p = (A/T) + B$. The vapour pressure, p_L^t of a given reaction mixture was derived by the equation,

$$p_L^t = N_{Ac_2O} \cdot p^t_{Ac_2O} + N_{(AcOH)_2} \cdot p^t_{(AcOH)_2},$$

where t is the temperature, and p represents vapour pressures of the pure liquids and N mole fractions. The data used were obtained from tables[14] and calculated values of p_L are given in Table I.

The second factor which demands the introduction of a correction is the solubility of the evolved carbon dioxide in the solvents. It has been shown in the succeeding paper[4] that the total number of moles of CO and CO_2 produced at any stage in the reaction is given by

$$n_{(CO+CO_2)} = \frac{(P-p_L)V_m}{RT} \cdot \frac{(2V+2V_L \cdot s_{CO_2})}{(2V+V_L \cdot s_{CO_2})},$$

where V_m is the measured volume increase and V is the total volume of gas in contact with the reaction mixture, $V° = V - V_m$, and V_L is the volume of the liquid reaction mixture. P is the total pressure on the gas phase, usually atmospheric, and s_{CO_2} is the molar ratio for the distribution of CO_2 between the gas phase and the solution.

V_L, V_m, P and T were measured for each run. The volume V° was determined by weighing the reaction vessel empty and then filled with distilled water at a known temperature; to the volume of the reaction vessel itself was added the contribution from the connecting tubes and the ungraduated portion of the burette, B, which were calculated from careful linear measurement of their dimensions. The appropriate value of p_L was obtained from Table I. Using the values of s_{CO_2} for acetic acid and acetic anhydride which are due to Just[15], the distribution ratio was obtained for mixtures by linear interpolation on a plot of s_{CO_2} against volume composition. The values obtained in this way are also given in Table I.

Errors

Nearly all the error in the experimental determination of specific reaction rate originates in the pipetting of the reactants. The pipette used for the oxalic acid solution was a 1 ml. "Technico" grade B with a maximum estimated reading error of 0·01 ml., corresponding to an error of 0·5 per cent in the concentration of 0·07 M. oxalic acid solutions and 3·5 per cent in that of 0·01 M. solutions. The errors are calculated for $V_L = 20$ ml., which was the value normally used. The pipettes used for acetic acid and acetic anhydride were 10 ml. "Gallenkamp" pipettes with an estimated reading

TABLE I

Per cent acetic anhydride v/v		0	20	40	60	80	90	100
Per cent acetic acid v/v		100	80	60	40	20	10	0
p_L (mm.)	25°C.	13·8	11·4	9·4	7·8	6·0	5·1	4·8
	30°C.	20·6	17·3	14·3	11·5	8·6	7·2	6·5
	35°C.	29·9	25·2	20·8	16·7	12·5	10·5	9·5
s_{CO_2}	25°C.	4·68	4·78	4·89	5·00	5·10	5·16	5·21
	30°C.	4·21	4·31	4·40	4·50	4·60	4·65	4·70
	35°C.	3·74	3·83	3·92	4·01	5·00	4·14	4·19

error of 0·1 ml., corresponding to an error of 0·6 per cent in the concentration for 90 per cent acetic anhydride solutions and 2·5 per cent for the 20 per cent solutions.

Error incurred by assuming additivity of volumes, and by assuming ideality in calculating vapour pressures and distribution ratios are considered to be negligible.

The stoichiometry of the reaction

Three solutions, all 0·05 M. with respect to oxalic acid, were allowed to react until the evolution of gas had apparently ceased. The gas yield was calculated as indicated above from the measured volume increase in the gas phase, with the following results:—

Per cent v/v $(AcOH)_2$ initially	60	10	0
Per cent v/v Ac_2O initially	40	90	100
Gas yield in moles, per mole of oxalic acid	1·86	2·01	1·94

When the concentration of acetic anhydride is low, the rate of gas evolution is very small towards the end of the reaction and it is difficult to determine when the reaction is effectively complete. This probably accounts for the low yield of gas in the case of reaction in 40 per cent acetic anhydride.

The results establish that the stoichiometric equation for the reaction is $(COOH)_2 - H_2O = CO + CO_2$, and also confirm the correctness of the procedure adopted in correcting for vapour pressure and the solubility of carbon dioxide.

Experimental rate determinations

By plotting for each reaction the volume of gas liberated at N.T.P. against the time and drawing tangents to the curves to obtain a quantity, v, proportional to the initial velocity of the reaction, a series of values of v were obtained for various oxalic acid and acetic anhydride concentrations. An approximate linear dependence of v on the oxalic acid concentration emerged, but no simple relationship between v and the acetic anhydride concentration could be found.

The use of v as a measure of the reaction rate proved quite unreliable. A point of inflexion near zero time on the reaction curve made it difficult to draw tangents reproducibly enough to give the slope within 5 per cent.

When $\log(a-X/2)$ was plotted against the time, where a is the initial number of moles of oxalic acid present, and X is the number of moles of products, a well-defined

straight line was obtained, from the slope of which a first order specific reaction rate could be determined. An initial kink in the curve, corresponding to the point of inflexion mentioned above, was evidently associated with a short time during which equilibrium was being established between gas and liquid phases.

Some runs were continued until 90 per cent of the reaction was over and the simple first order relationship was accurately applicable throughout. Examples are given in Fig. 2, where the plot of $\log(a-X/2)$ against time is given for three different runs.

The experimental rate determinations for a series of acetic acid-acetic anhydride mixtures, a range of oxalic acid concentrations and three different temperatures are summarized in Tables II, III and IV. Experiment numbers are given in parenthesis after each specific reaction rate.

It is apparent from the tables that, for any given acetic acid-acetic anhydride mixture, the first order specific rate for the disappearance of oxalic acid is in fact a constant, independent of the oxalic acid concentration up to at least 0·07 M.

The concentration of acetic anhydride is so much greater than that of oxalic acid that no significant error is incurred by interpreting the results as a first order disappearance of oxalic acid and ignoring the fact that acetic anhydride is consumed simultaneously.

TABLE II (30°C.)

Per cent v/v Ac_2O	20	40	60	80	90
Per cent v/v $(AcOH)_2$ ..	80	60	40	20	10
c_{Ac_2O} (mole/litre)	2·12	4·24	6·36	8·48	9·54
$c_{(AcOH)_2}$ (moles/litre) ..	7·00	5·25	3·50	1·75	0·88
$c_{(COOH)_2}$ mole/litre	$10^5 \times$ first order specific reaction rate. (sec.$^{-1}$.)				
0·01	6·95 (1)	—	—	—	30·7 (33) 30·1 (34)
0·02	7·11 (2) 7·26 (3)	—	22·5 (18)	—	30·1 (36)
0·03	7·21 (4)	15·9 (10)	—	—	29·5 (37) 30·8 (38)
0·04	—	16·4 (11) 16·4 (12)	23·5 (21)	29·5 (28)	30·1 (39)
0·05	7·37 (6)	16·2 (13)	22·5 (23)	29·4 (29)	30·4 (40) 30·5 (41)
0·06	7·59 (7)	15·8 (14)	23·1 (24) 23·7 (25)	28·7 (30)	30·1 (42)
0·07	7·69 (8)	15·8 (15) 16·2 (16)	23·4 (26) 22·6 (27)	28·8 (31) 29·0 (32)	30·4 (43) 30·4 (44)
Mean	7·31	16·1	23·0	29·1	30·3
Mean deviation	0·2	0·2	0·4	0·3	0·3
Probable error of the mean ..	0·1	0·1	0·2	0·1	0·1

TABLE III (25°C.)

Per cent v/v Ac_2O	20	90
Per cent v/v $(AcOH)_2$ ..	80	10
c_{Ac_2O} (moles/litre)	2·12	9·54
$c_{(AcOH)_2}$ (moles/litre)	7·00	0·88
$c_{(COOH)_2}$ (moles/litre)	$10^5 \times$ specific rate. (sec.$^{-1}$.)	
0·02	4·3 (45)	16·5 (51)
0·03	4·1 (46)	17·2 (52)
0·04	3·8 (47)	16·8 (53)
0·05	4·2 (48)	17·0 (54)
0·06	4·0 (49)	17·8 (55)
0·07	4·3 (50)	18·0 (56)
Mean	4·1	17·2
Mean deviation	0·2	0·4
Probable error of the mean ..	0·1	0·2

TABLE IV (35°C.)

Per cent v/v Ac_2O	20	90
Per cent v/v $(AcOH)_2$ ..	80	10
c_{Ac_2O} (moles/litre)	2·12	9·54
$c_{(AcOH)_2}$ (moles/litre)	7·00	0·88
$c_{(COOH)_2}$ (moles/litre)	$10_5 \times$ specific rate. (sec.$^{-1}$.)	
0·02	12·4 (57)	—
0·03	12·8 (58)	—
0·04	13·2 (59)	—
0·05	12·8 (60)	52·4 (63)
0·06	12·8 (61)	52·5 (64)
0·07	13·1 (62)	52·0 (65)
Mean	12·9	52·3
Mean deviation	0·2	0·2
Probable error of the mean ..	0·1	0·1

Activation energy

Activation energies were calculated according to the equation of Arrhenius for olutions of 20 per cent and 90 per cent v/v acetic anhydride content and for a temperature range of 25°C. to 35°C. The equations

$$\ln j = -E/RT + \text{const.}$$
$$\text{and} \quad \ln j' = -E/RT' + \text{const.},$$

where j and j′ are the experimental first order specific rates at the absolute temperatures T and T′, give

$$E = \left(R \ln \frac{j}{j'} \right) \Big/ \left(\frac{1}{T'} - \frac{1}{T} \right)$$

The calculation was carried out for T′=303·2°A., T=298·2°A. and for T′=308·2°A., T=303·2°A. The results are given in Table V. The mean value of the four results is 20·6 k. cal. deg.$^{-1}$mole^{-1}, with a mean deviation of 0·2 k. cal. It is noteworthy that there is no signicant difference between the activation energies obtained with the two different solvent mixtures.

Empirical rate equations

Three simple graphical representations showing the dependence of reaction rate on the acetic anhydride content of the solution are possible.

(i) $$j = 3{\cdot}52 \times 10^{-5} . c_{Ac_2O} \quad (30°C.).$$

This is evident from Fig. 3, where the specific reaction rate is plotted against the concentration of acetic anhydride. The relationship holds for solutions containing up to 80 per cent v/v of the anhydride. The mean deviation of the values of j calculated by (i) from the experimental results is 0·08 and the deviations are all less than the estimated experimental uncertainty.

(ii) $$j = 4{\cdot}85 \times 10^{-2} . \eta . N_{Ac_2O} - 3{\cdot}71 \times 10^{-5} \quad (30°C.).$$

The appropriate plot, of specific rate against the product of the viscosity of the medium and the acetic anhydride mole fraction, is given in Fig. 4. The equation applies over the same range as (i).

The viscosities of the different acetic acid-acetic anhydride mixtures were computed with the aid of Kendall's equation[16],

$$\log \eta = N_{Ac_2O} \cdot \eta_{Ac_2O} + N_{(AcOH)_2} \cdot \eta_{(AcOH)_2}.$$

The applicability of the equation was confirmed by comparing the calculated values for mixtures of acetic acid and acetic anhydride at 15°C. with the experimental values given in the International Critical Tables[17]. In calculating the viscosities of mixtures at 30°C., the viscosities of acetic acid and acetic anhydride were taken as 1·04 and 0·783 centipoise respectively at that temperature[18]. Experimental and calculated viscosities are given in Table VI.

TABLE V

	Per cent v/v acetic anhydride	20	90
E	303·2°A. – 298·2°A.	20·49	20·42
(k cal. mole^{-1}deg.$^{-1}$)	308·2°A. – 303·2°A.	20·94	20·57

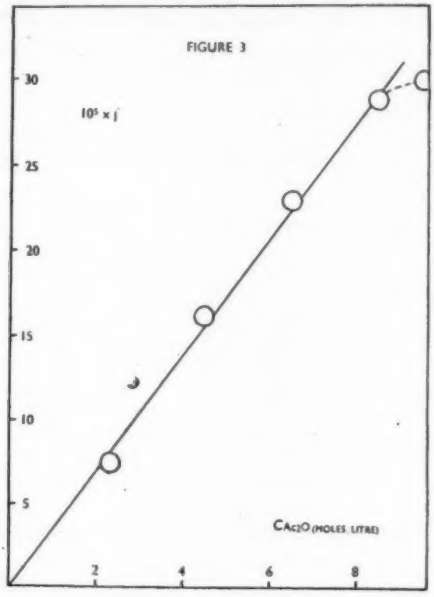
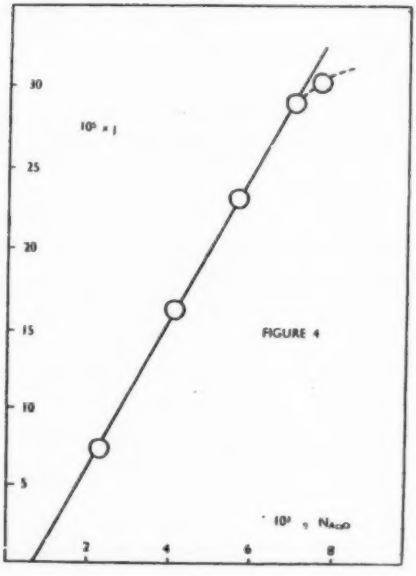
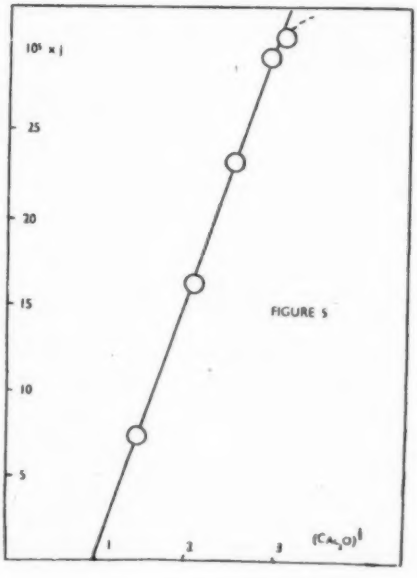


FIGURE 3
$10^5 \times j$
30
25
20
15
10
5
2
4
6
8
C_{Ac_2O} (MOLES/LITRE)


$10^5 \times j$
30
25
20
15
10
5
FIGURE 4
2
4
6
8
$10^2 \times N_{Ac_2O}$


$10^5 \times j$
25
20
15
10
5
FIGURE 5
1
2
3
$(C_{Al_2O})^{\frac{1}{2}}$

(iii) $$j = 1{\cdot}48 \times 10^{-4}(c_{Ac_2O})^{\frac{1}{2}} - 1{\cdot}44 \times 10^{-4} \quad (30°C.).$$

The appropriate plot, showing that the equation is applicable again over the range up to 80 per cent acetic anhydride, is given in Fig. 5.

The effect of viscosity on the reaction rate

Since the empirical equation (ii) involves a viscosity term and resembles superficially the equation of Moelwyn-Hughes[19] calculated on the basis of a simple collision theory applied to reactions in solution, *viz.*,

$$\text{Rate} = P(3\pi/4)\,(r_A+r_B)\left(\frac{1}{m_A}+\frac{1}{m_B}\right).\frac{n_An_B}{n_A+n_B+n_C}.\eta\,.\exp(-E/RT),$$

it was deemed advisable to study the effect of the viscosity of the medium on the reaction rate. This was done as follows:—

0·60 g. of "Perspex" was dissolved in 50 ml. of acetic anhydride and a viscous stock solution was obtained. Reaction mixtures of varying viscosity were prepared by adding different volumes of this stock solution in place of unthickened acetic anhydride. After the reaction rate had been measured with a particular mixture, the viscosity of the latter relative to that of the corresponding normal mixture was determined with the aid of an Ostwald viscometer. The results of these experiments are summarized in Table VII. Despite the fact that the use of thickened solutions increased the pipetting errors, it is clearly seen that the viscosity of the medium has no significant effect on the reaction rate.

The effect of mineral acid and potassium acetate on the rate

Comparative experiments showed that sulphuric acid and potassium acetate both cause a considerable increase in the reaction rate. The catalyses are complicated by side reactions; that with sulphuric acid by the attendant formation of sulphoacetic acid and that with potassium acetate by a precipitation reaction. Pending more detailed investigations, it is sufficient to record here the mere fact of catalysis.

DISCUSSION

The simplest and most obvious mechanism which may afford an explanation of the experimental facts is a bimolecular reaction between oxalic acid and acetic anhydride. This reaction will be considered firstly on the basis of the collision theory and then on the basis of the transition state theory.

TABLE VI

15°C.	N_{Ac_2O}	0	0·115	0·336	0·540	0·733	0·913	1·00
	η(experimental)	·0133	·0132	·0119	·0113	·0106	·0101	·0098
	η(calculated)	—	·0128	·0120	·0113	·0106	·0101	—
30°C.	Per cent v/v Ac_2O	0	20	40	60	80	90	100
	N_{Ac_2O}	0	·232	·447	·648	·829	·915	1·00
	η(experimental)	·0104	—	—	—	—	—	·00783
	η(calculated)	—	·00975	·00918	·00863	·00822	·00800	—

Equation (iii), involving the square root of the acetic anhydride concentration seems to be merely an empiricism and it has not been possible to assign to it a theoretical significance.

Moelwyn-Hughes[19] shows that the frequency, ${}_AZ_B$, of binary collisions between solute molecules, A and B, of comparable dimensions in the presence of solvent molecules, C, is

$$ {}_AZ_B = (3\pi\eta/4)\,(r_A+r_B)\left(\frac{1}{m_A}+\frac{1}{m_B}\right)\cdot\left(\frac{n_An_B}{n_A+n_B+n_C}\right), $$

where n represents concentrations in molecules cm.$^{-3}$, r collision radii, m molecular masses and η viscosity. The rate of the reaction between A and B would then be

$$ P\,.\,{}_AZ_B\,.\exp(-E/RT), $$

where E is the energy of activation and P the probability factor. For the reaction between oxalic acid and acetic anhydride, if we neglect the concentration of oxalic acid compared with that of acetic anhydride, we obtain

$$ \text{Rate} = P(3\pi\eta/4)\,(r_{(COOH)_2}+r_{Ac_2O})\left(\frac{1}{m_{(COOH)_2}}+\frac{1}{m_{Ac_2O}}\right)\cdot $$

$$ \cdot\left(\frac{n_{(COOH)_2}\cdot n_{Ac_2O}}{n_{Ac_2O}+n_{(AcOH)_2}}\right).\exp(-E/RT). $$

But we have also

$$ \text{Rate} = j\,.\,c_{(COOH)_2}, $$

so that the specific reaction rate may be written

$$ j = P(3\pi\eta/4)\,(r_{(COOH)_2}+r_{Ac_2O})\left(\frac{1}{m_{(COOH)_2}}+\frac{1}{m_{Ac_2O}}\right).N_{Ac_2O}\,.\exp(-E/RT) $$

and the plot of j against $\eta\,.N_{Ac_2O}$ should be a straight line. This is in accord with the empirical equation (ii), although the collision theory affords no explanation of the intercept in the plot of j against $\eta\,.N_{Ac_2O}$. If the intercept is ignored (though this is certainly not a valid procedure, since the intercept cannot be ascribed to experimental errors), then, by comparing the experimental and theoretical equations, we obtain, for P=1,

$$ r_{(COOH)_2} + r_{Ac_2O} = 1{\cdot}16 \times 10^{-9}\ \text{cm}. $$

Alternatively, by taking the values for atomic radii given by Moelwyn-Hughes[20] and drawing out the oxalic acid and acetic anhydride molecules, we find that the sum of the radii is $7{\cdot}2\times10^{-8}$ cm., which corresponds to a value for P of $1{\cdot}6\times10^{-2}$.

This is in accord with general experience in the application of the collision theory. The reaction is "normal", as is generally the case with reactions having an activation energy of about 20 k. cal.[21].

TABLE VII (30°C.)

Reaction mixture: 40 *per cent v/v acetic anhydride*; 60 *per cent v/v acetic acid.* 0·03 *M in oxalic acid.*

g. "Perspex" per litre ..	0	1·2	1·8	3·0
10^5 × specific rate (sec.$^{-1}$) ..	15·9	15·3	15·3	15·8
Relative viscosity	1·00	1·45	1·68	2·24

The presence of the intercept in the plot of j against $\eta . N_{Ac_2O}$ implies, however, that an interpretation (such as the above) in terms of the collison theory must be an oversimplification. In addition, the fact that the reaction rate is independent of the viscosity again emphasises the need for caution in applying the concept of macroscopic viscosity to the movement of molecules in an environment of other molecules.

The bimolecular process may be represented as follows:—

$$(COOH)_2 + Ac_2O \underset{\longleftarrow}{\overset{K^*}{\rightleftharpoons}} X^*, X^* \longrightarrow \text{products.}$$

K* is defined by the equations

$$K^* = \frac{a_{X^*}}{a_{(COOH)_2} . a_{Ac_2O}} = \exp(-\triangle G^*/RT),$$

where X* is an activated complex, a_{X^*}, $a_{(COOH)_2}$ and a_{Ac_2O} are the activities of the activated complex, oxalic acid and acetic anhydride respectively, and $\triangle G^*$ is the thermodynamic potential increment of activation. The specific reaction rate for the first order disappearance of oxalic acid is then given by[22]

$$j = (W . kT/h) . K^* . \frac{f_{(COOH)_2} . f_{Ac_2O}}{f_{X^*}} . c_{Ac_2O},$$

where W is the transmission coefficient, k is Boltzmann's constant, T is the absolute temperature and the f are activity coefficients. If W and the f are taken to be unity, then comparison with the empirical equation (i) gives

$$(kT/h) . K^* = 3{\cdot}52 \times 10^{-5}.$$

But[23], $(kT/h) . K^* = (kT/h) . \exp(-\triangle H^*/RT) . \exp(\triangle S^*/R)$

and $\triangle H^* = E - RT$, where E is the energy of activation.
It follows then that

$$(kT/h)K^* = (e . kT/h) . \exp(\triangle S^*/R) . \exp(-E/RT),$$

and, since $(kT/h)K^*$ is known and the activation energy, E, is determined as 20·6 k. cal., the frequency factor, $(e . kT/h) . \exp(\triangle S^*/R)$, may be calculated and is found to be $2{\cdot}5 \times 10^{10}$.

The entropy of activation may readily be calculated from this value for the frequency factor, and is found to be

$$\triangle S^* = -22{\cdot}2 \text{ cal. deg.}^{-1} \text{ mole.}^{-1}.$$

The transition state theory, therefore, appears to give an exhaustive explanation of the experimental facts. It has not been possible, within the scope of this work, to make a study of the equilibrium $AcOH_2^+ + Ac_2O = Ac^+ + (AcOH)_2$, but now that the mechanism of the uncatalysed dehydration of oxalic acid has been elucidated it may be possible to use the catalysed reaction in a study of acid-base equilibria of this type.

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THE DETERMINATION OF THE RATE OF A REACTION IN SOLUTION BY MEASUREMENTS ON GASEOUS REACTANTS OR PRODUCTS WHICH ARE APPRECIABLY SOLUBLE IN THE REACTION MIXTURE

by

W. B. ENGLAND and H. A. E. MACKENZIE

OPSOMMING

Daar word teoreties bewys dat die voortgang van 'n reaksie in oplossing waargeneem kan word deur meting van die volume of druk van die gesagtige reagense of produkte, selfs wanneer sommige van die reagense of produkte redelik oplosbaar in die reaksie-mengsel is. Oor die algemeen is 'n analise van die gasfase gedurende die opeenvolgende stadia van die reaksie nodig. Hierdie tydrowende proses kan in sekere gevalle waar die stoichiometrie van die reaksie bekend is, vermy word.

SUMMARY

It is shown theoretically that the progress of a reaction in solution may be followed by volume or pressure measurements of gaseous reactants or products even when some of these are appreciably soluble in the reaction mixture. In general an analysis of the gas phase is required at successive stages during the course of the reaction, but this tedious process may be avoided in certain cases where the stoichiometry of the reaction is known.

The progress of a reaction in solution is often followed most conveniently by measuring the volume or pressure of a gas absorbed or evolved during the reaction. The technique has proved especially useful and accurate in the study of auto-oxidations[1], where gaseous oxygen is absorbed during the course of reaction, of dehydrations[2], where carbon monoxide is liberated, and of the decomposition of diazo compounds[3] which is accompanied by the evolution of nitrogen. In such cases the gaseous reactant or product is so slightly soluble in the reaction mixture that the volume of gas at constant pressure or the pressure on the gas at constant volume may be taken as a measure of the extent of reaction, provided that a correction is applied for the vapour pressure of the reaction mixture.

Sometimes, however, the gaseous product or reactant readily dissolves in the reaction mixture so that the volume or pressure of the gas no longer provides in general a direct measure of the extent of reaction. This is particularly the case with carbon dioxide which is appreciably soluble in most oxygen-containing solvents. Schierz[4], for example, mentions that oxalic acid is decomposed by acetic anhydride in the presence of nitrogen bases, but states that unequal volumes of carbon monoxide and carbon dioxide are liberated during the reaction due to their differing solubilities; and for this reason, apparently, has not investigated further the kinetics of the reaction.

Yet the problem is by no means difficult of solution. During their study of an allied reaction, the uncatalysed dehydration of oxalic acid in acetic acid-acetic anhydride mixtures[5], the authors have been obliged to examine the implications of the solubility of carbon dioxide in order to interpret measured gas volumes in terms of the extent of the reaction. It has seemed worthwhile to deal with the problem generally.

For simplicity the gas phase is regarded as ideal which is a reasonably good approximation under ordinary laboratory conditions. It is convenient to make use of a distribution ratio, s, defined by

$$s = c_L/c_G, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where c_L is the concentration of a substance in solution in the liquid phase and c_G is its concentration in the gas phase, both expressed in moles litre^{-1}. Just[6] has used

the distribution ratio in recording the results of his determinations on the solubility of various gases in organic liquids. The ratio is a constant for a particular gas and liquid at a given temperature. It will be assumed that several soluble gases present together in one system will have no mutual effect on one another's distribution ratios and that these ratios will be unaffected by the presence of non-volatile solutes in the liquid phase. These assumptions must be applied with caution in practical cases, but will approximate closely to the truth if all concentrations in the liquid phase are small.

We shall consider a reaction proceeding at constant temperature. The disappearance of a reactant in solution, it is assumed, will be accompanied by the formation (or disappearance) of several gases, A_i, which have distribution ratios, s_i.

The interpretation of gas volumes measured at constant pressure

Let V^0 litres be the total initial volume of gas in contact with the reactant solution and let V litres be the subsequent total volume of gas after t seconds, at which time, it will be assumed, n_i moles of each of the A_i will have been formed (or removed). The problem is to calculate Σn_i from the measured volume increase.

The constant pressure on the gases, P atmospheres, is given by

$$P = \Sigma P_j + P_L + \Sigma P_i, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where P_j are the partial pressures of gases, A_j, not participating in the reaction, but assumed to have been present initially in the reaction vessel, P_L is the vapour pressure of the reaction mixture and the P_i are the partial pressures of the reactant or product gases. P_L will, in the case of dilute solutions, be approximately equal to the vapour pressure of the solvent and remain constant throughout the reaction.

The number of moles of A_i in the gas phase is P_iV/RT, so that

$$(c_G)_i = P_i/RT \text{ moles/litre} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$(c_L)_i = (c_G)_i . s_i = P_i s_i/RT \text{ moles/litre.} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If V_L is the volume of the reaction mixture in litres, then the number of moles of A_i in solution is $P_i . s_i . V_L/RT$. The total number of moles of A_i in the system is thus

$$n_i = P_i(V + s_i . V_L)/RT. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The measured volume increase during t seconds is

$$V_m = V - V^0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

and therefore, from equations (5) and (6),

$$n_i = P_i(V_m + V^0 + s_i V_L)/RT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

and

$$\Sigma n_i = (V_m + V^0) . \Sigma P_i/RT + V_L . \Sigma s_i P_i/RT. \quad \ldots\ldots\ldots\ldots\ldots (8)$$

Substitution of equation (2) in (8) gives

$$\Sigma n_i = (V_m + V^0)(P - \Sigma P_j - P_L)/RT + V_L . \Sigma s_i P_i/RT. \quad \ldots\ldots\ldots (9)$$

Since the number of moles of gases not participating in the reaction remains constant, it is possible to evaluate ΣP_j. If n_j is the total number of moles of each of the A_j in the system then, initially,

$$\Sigma n_j = \Sigma P_j(V^0 + s_i V_L)/RT, \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where s_j is the distribution ratio for a gas A_j. Since ΣP_i is zero initially, we have from equations (2) and (10),

$$\Sigma n_j = (P-P_L)\,(V^0+s_j^*.V_L)/RT, \quad \ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where
$$s_j^* = \Sigma n_j s_j/\Sigma n_j. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

After t seconds

$$\Sigma n_j = (V+s_j^*.V_L).\Sigma P_j/RT, \quad \ldots\ldots\ldots\ldots\ldots\ldots(13)$$

and elimination of Σn_j between equations (11) and (13) gives

$$\Sigma P_j = (P-P_L)\,(V^0+s_j^*.V_L)/(V+s_j^*.V_L). \quad \ldots\ldots\ldots\ldots\ldots(14)$$

Substitution of this value for ΣP_j in equation (9) yields the result

$$\Sigma n_i = (P-P_L)\left(\frac{V.V_m}{V+s_j^*.V_L}\right)/RT + V_L.\Sigma s_i P_i/RT. \quad \ldots\ldots\ldots(15)$$

The first term on the right hand side of the equation gives the number of moles of the A_i in the gas phase and the second term gives the number of moles in solution.

The former is readily calculated from the experimentally measureable quantities, P, P_L, V, V_m, V_L, T and s_j^*. The latter may be obtained in general by an analysis of the gases collected at time t and the experimental determination of the s_i.

This somewhat tedious process may be avoided in certain cases. We may consider, for example, the dehydration of oxalic acid in acetic acid-acetic anhydride mixtures. The reaction may be followed by volumetric measurement of the evolved carbon monoxide and carbon dioxide at constant pressure. Air, which may be present initially in the apparatus, but which does not enter into the reaction, has $s_j^* \sim O$ for both acetic acid and acetic anhydride[6], so that equation (15) becomes

$$n_{(CO+CO_2)} = (P-P_L).V_m/RT + V_L(s_{CO}.P_{CO}+s_{CO_2}P_{CO_2})/RT.$$

Since $s_{CO} \sim O$, we have

$$n_{(CO+CO_2)} = (P-P_L).V_m/RT + V_L.s_{CO_2}.P_{CO_2}/RT. \quad \ldots\ldots\ldots(16)$$

In addition, we have from equation (5),

$$n_{CO_2} = P_{CO_2}(V+s_{CO_2}.V_L)/RT,$$

and from the stoichiometry of the reaction, therefore,

$$n_{(CO+CO_2)} = 2.P_{CO_2}(V+s_{CO_2}.V_L)/RT,$$

or,
$$P_{CO_2} = n_{(CO+CO_2)}.RT/(2V+2V_L.s_{CO_2}), \quad \ldots\ldots\ldots\ldots\ldots(17)$$

so that, by substituting (17) in (16), we obtain

$$n_{(CO+CO_2)} = \frac{(P-P_L).V_m}{RT}.\left(\frac{2V+2V_L.s_{CO_2}}{2V+V_L.s_{CO_2}}\right). \quad \ldots\ldots\ldots\ldots(18)$$

The number of moles of CO and CO_2 produced, and thus the number of moles of oxalic acid decomposed, may be calculated from the measured volumes and pressure, provided that the vapour pressure of the solvent and the distribution ratio for carbon dioxide are known. The kinetics of the reaction, therefore, may be investigated by volumetric measurement of the evolved gases.

The interpretation of gas pressures measured at constant volume

Let P^0 atmospheres be the initial pressure on the gas in contact with the reaction mixture and let P atmospheres be the pressure after t seconds. The constant total gas volume is taken as V litres.

As before, equation (2) is applicable, but in this case both ΣP_j and P_L remain constant. Since ΣP_j is zero initially,

$$P_m = P - P^0 = \Sigma P_j. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

From equation (5), we have in this case

$$\Sigma n_i = (V \cdot \Sigma P_i + V_L \cdot \Sigma s_i P_i)/RT = \frac{P_m \cdot V}{RT} + \frac{V_L \cdot \Sigma s_i P_i}{RT}. \quad \ldots\ldots\ldots(20)$$

Again, an analysis of the gas phase is generally required for the evaluation of the second term on the right of the equation, but this may be avoided in some cases as before.

In the dehydration of oxalic acid in acetic acid-acetic anhydride mixtures, for example, the stoichiometry of the reaction enables one to obtain, from equation (20),

$$n_{(CO+CO_2)} = \frac{P_m \cdot V}{RT} \cdot \left(\frac{2V + 2V_L \cdot s_{CO_2}}{2V + V_L \cdot s_{CO_2}} \right), \quad \ldots\ldots\ldots\ldots(21)$$

which is identical in form with equation (18).

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THE REACTION BETWEEN CINNAMIC ACID AND CERTAIN PHENOLS

by

J. D. M. SIMPSON and S. S. ISRAELSTAM

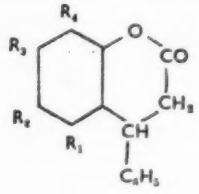
OPSOMMING

Kaneelsuur is met verskeie fenole in die teenwoordigheid van swawelsuur gekondenseer om derivate van 4-feniel-3 : 4-dihiedrokumarien te berei. Die bereiding van die sinnamate van verskeie fenole word ook beskryf.

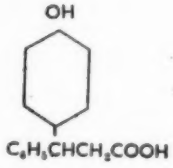
SUMMARY

Cinnamic acid has been condensed with various phenols in the presence of sulphuric acid to give derivatives of 4-phenyl-3 : 4-dihydrocoumarins. The preparation of certain phenolic cinnamates is also described.

Liebermann and Hartmann [1a, b, c] investigated the condensation of cinnamic acid and allo-cinnamic acid with phenols. With phenol, after three hours, they obtained 4-phenyl-3 : 4-dihydrocoumarin (**I**, $R_1 = R_2 = R_3 = R_4 = H$) and β-phenyl-β-(p-hydroxyphenyl)-propionic acid (**II**).



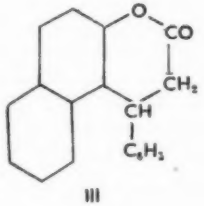
I



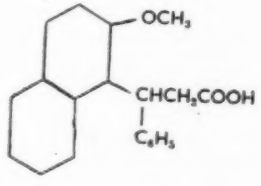
II

Resorcinol and hydroquinone when condensed with either acid gave respectively 7-hydroxy-4-phenyl-3: 4-dihydrocoumarin (**I**, $R_1 = R_2 = R_4 = H$; $R_3 = OH$) and 6-hydroxy-4-phenyl-3: 4-dihydrocoumarin (**I**, $R_1 = R_3 = R_4 = H$; $R_2 = OH$), whilst catechol could only be condensed with allo-cinnamic acid to give 8-hydroxy-4-phenyl-3: 4-dihydrocoumarin (**I**, $R_1 = R_2 = R_3 = H$; $R_4 = OH$).

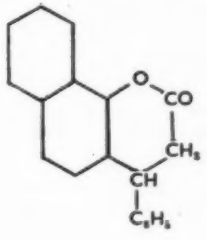
Koelsch[2] condensed cinnamic acid with β-naphthol to give 4-phenyl-3: 4-dihydro-5: 6-benzocoumarin (**III**) which was then converted to β-phenyl-β-(2-methoxy-naphthyl-1)-propionic acid (**IV**).



III



IV



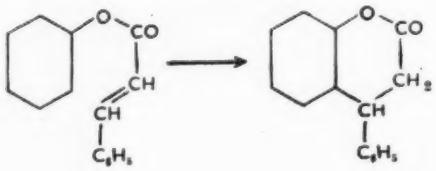
V

The constitution of these compounds is proved by the synthesis of 4-phenyl-3: 4-dihydrocoumarin by Greenwood and Nierenstein[3] from *o*-methoxy-benzhydrol and ethyl malonate followed by demethylation and ring-closure of the resulting β-phenyl-β-(*o*-methoxyphenyl)-propionic acid, and by the preparation of 5: 7-dihydroxy-4-phenyl-3: 4-dihydrocoumarin (**I**, $R_1 = R_3 = OH$; $R_2 = R_4 = H$) from phloroglucinol and cinnamonitrile by Fischer and Nouri[4]. Further, both 4-phenyl-3: 4-dihydrocoumarin and 5: 7-dihydroxy-4-phenyl-3: 4-dihydrocoumarin have been prepared by the reduction of the corresponding coumarins [1, 4].

In the present investigation it was found that when cinnamic acid and phenol in glacial acetic acid were treated with concentrated sulphuric acid according to the details given by Liebermann and Hartmann, a maximum yield of 18 per cent of 4-phenyl-3: 4-dihydrocoumarin only was obtained, and no β-phenyl-β-(*p*-hydroxyphenyl)-propionic acid could be isolated, although the experiment was repeated several times. Owing to the large excess of sulphuric acid used it was thought that the poor yields were due to sulphonation of the reaction products. It was decided, therefore, to heat equimolecular quantities of phenol and cinnamic acid with varying amounts of concentrated sulphuric acid (1 drop to 1 ml. for 2·5 grams of cinnamic acid) in the absence of a solvent. When 1 drop of concentrated sulphuric acid was used a small amount of phenyl cinnamate was obtained, but no dihydrocoumarin could be isolated. The use of large volumes of concentrated sulphuric acid led to the extensive charring of the products. It was found that by heating with 0·5 ml. of acid for 15 minutes, the yield of dihydrocoumarin was 11 per cent, but after 30 minutes or one hour the yield was 20 per cent. This modified technique shortened the time required for condensation by two hours. Although an excellent yield was obtained of the dihydrocoumarin from *p*-cresol (92 per cent) and moderate yields from hydroquinone (37 per cent) and *m*-cresol (54 per cent) poor yields were obtained from the other phenols.

The following dihydrocoumarins were prepared by this modified method: 8-*methyl*-4-*phenyl*-3: 4-*dihydrocoumarin* (**I**, $R_4 = CH_3$; $R_1 = R_2 = R_3 = H$); 7-*methyl*-4-*phenyl*-3: 4-*dihydrocoumarin* (**I**, $R_3 = CH_3$; $R_1 = R_2 = R_4 = H$); 6-*methyl*-4-*phenyl*-3: 4-*dihydrocoumarin* (**I**, $R_2 = CH_3$; $R_1 = R_3 = R_4 = H$); 4-*phenyl*-3: 4-*dihydro*-7: 8-*benzocoumarin* (**V**); 4-phenyl-3: 4-dihydro-5: 6-benzocoumarin (**III**) and 4-phenyl-6-hydroxy-3: 4-dihydrocoumarin (**I**, $R_2 = OH$; $R_1 = R_3 = R_4 = H$). The first four have not been described before.

All attempts to prepare 4-phenyl-7-hydroxy-3: 4-dihydrocoumarin from cinnamic acid and resorcinol, either by the original method of Liebermann and Hartmann[1a], or by the modified method, led to the formation of intractable, red, tarry materials which could not be purified. Similar results were obtained with catechol.



An interesting point worth noting was that when the cinnamate esters of the corresponding phenols were heated with 70 per cent sulphuric acid for about half an hour, the dihydrocoumarins were obtained in similar yields. At first it was thought that cyclization of the cinnamate had occurred, addition taking place between the ortho-carbon in the phenolic ring and the β-carbon in the cinnamic residue (see equasion on page 166).

Further experiments showed that actually the cinnamate is first hydrolysed to the phenol and cinnamic acid and that these compounds then react with each other under the influence of the sulphuric acid to give the dihydrocoumarin.

The dihydrocoumarins, with the exception of the 6-hydroxy-compound, are insoluble in cold aqueous sodium hydroxide, but dissolve on boiling to give colourless solutions which do not exhibit fluorescence. Similarly, they dissolve in concentrated sulphuric acid to give colourless solutions without fluorescence. The failure of dihydrocoumarins to exhibit fluorescence has been noted by other workers[6].

The phenolic cinnamates were prepared in excellent yield (over 85 per cent) by modifying the method of Womack and McWhirter[5] who condensed cinnamoyl chloride with the phenol. One of the cinnamates prepared by this modified method, 3-*methoxyphenyl cinnamate*, has not been described before.

As mentioned above the reaction between equimolecular amounts of phenol and cinnamic acid in the presence of one drop of concentrated sulphuric acid yielded a small quantity of phenyl cinnamate. It was found that when one drop of concentrated sulphuric acid was added to a solution of cinnamic acid and phenol in acetic anhydride there was a rise in temperature of 30°C.; on further heating the solution at 150°C. for one hour, a 30 per cent yield of phenyl cinnamate was obtained, together with cinnamic acid and phenyl acetate. The first stage in this reaction must be the formation of cinnamic anhydride by the interaction of cinnamic acid and acetic anhydride:—

$$2\,C_6H_5CH = CHCOOH + (CH_3CO)_2O \longrightarrow (C_6H_5CH = CHCO)_2O + 2\,CH_3COOH,$$

since cinnamic anhydride was formed in 90 per cent yield by refluxing cinnamic acid and acetic anhydride in the presence of one drop of concentrated sulphuric acid. The second stage must be the interaction of cinnamic anhydride and the phenol to give the cinnamate:—

$$(C_6H_5CH = CHCO)_2O + C_6H_5OH \longrightarrow C_6H_5O.COCH = CHC_6H_5 + C_6H_5CH = CHCOOH.$$

In fact it was shown that an almost 100 per cent yield of the phenolic cinnamate could be obtained by heating together equimolecular quantities of the phenol and cinnamic anhydride at 150°C. with one drop of concentrated sulphuric acid.

A new cinnamate, *viz.*, 3-*acetoxyphenyl cinnamate*, was obtained from resorcinol, cinnamic acid and acetic anhydride, identical with that obtained from resorcinol, cinnamoyl chloride and pyridine. It was not possible to prepare resorcinol monocinnamate by any of the above methods, although resorcinol dicinnamate was obtained readily.

An interesting observation was the fact that phenyl acetate when heated with cinnamic acid in the presence of one drop of concentrated sulphuric acid gave a 50 per cent yield of phenyl cinnamate according to the equation:—

$$C_6H_5CH = CHCOOH + C_6H_5O.COCH_3 \longrightarrow C_6H_5CH = CHCOOC_6H_5 + CH_3COOH.$$

TABLE I

Phenol used	*Substituted* 3 : 4-*dihydrocoumarin obtained*	*Yield per cent*		*m.p.°C.*	*Formula*	*ANALYSIS*				*Ref.*
						Found		*Calculated*		
		a	*b*			*Per cent C*	*Per cent H*	*Per cent C*	*Per cent H*	
Phenol	4-phenyl	20	17	81 – 82	$C_{15}H_{12}O_2$	80·27	5·34	80·33	5·40	1(a), 3
o-Cresol	4-phenyl-8-methyl-	21	20	105 – 106	$C_{16}H_{14}O_2$	80·49	5·83	80·65	5·92	—
m-Cresol	4-phenyl-7-methyl-	54	59	120 – 121	$C_{16}H_{14}O_2$	80·79	6·07	80·65	5·92	—
p-Cresol	4-phenyl-6-methyl-	92	83	80 – 81	$C_{16}H_{14}O_2$	80·58	5·97	80·65	5·92	—
α-Naphthol ..	4-phenyl-7 : 8-benzo-	22	22	110 – 111	$C_{19}H_{14}O_2$	82·96	5·29	83·19	5·14	—
β-Naphthol ..	4-phenyl-5 : 6-benzo-	17	16	115 – 116	$C_{19}H_{14}O_2$	82·84	5·24	83·19	5·14	2
Hydroquinone ..	4-phenyl-6-hydroxy-	37	—	132 – 133	$C_{15}H_{12}O_3$	75·08	5·20	74·98	5·04	1(b)

EXPERIMENTAL

Preparation of 4-phenyl-3 : 4-dihydrocoumarins

(*a*) *From the phenol and cinnamic acid*

An equimolecular mixture of cinnamic acid and the phenol was mixed with concentrated sulphuric acid (0·2 ml. per gram of cinnamic acid), and heated in an oil-bath at 130°C. – 140°C. for thirty minutes. On pouring into water, a reddish-brown gum separated out. This was dissolved in ether and extracted with cold dilute sodium carbonate solution. Evaporation of the ether deposited dark-coloured oils which solidified on standing, or on treatment with ethanol. The crude products were crystallized from ethanol after treatment with charcoal.

The alkaline extracts on acidification deposited resinous products which proved difficult to purify.

(*b*) *From phenolic cinnamates*

A mixture of 5 grams of the finely powdered cinnamate and 5 ml. of 70 per cent sulphuric acid was heated for half an hour under reflux. The reaction product was poured into water and the reddish oil which separated was triturated with cold saturated sodium bicarbonate solution, and the insoluble dihydrocoumarin purified by crystallization.

Preparation of the phenolic cinnamates

(*a*) *From cinnamoyl chloride*

An equimolecular mixture of cinnamic acid and thionyl chloride was placed in a 250 ml. round-bottomed flask fitted with a reflux condenser carrying a calcium chloride tube. The mixture was heated on a boiling water-bath until evolution of hydrogen chloride ceased and cooled. A molecular proportion of the phenol was added, and the mixture returned to the water-bath. After the further evolution of hydrogen chloride the reaction mixture was transferred to a sand-bath and brought to the reflux temperature in order to remove the hydrogen chloride more completely. The reaction mixture was poured into water when a solid separated out. The latter was triturated with a cold saturated solution of sodium bicarbonate and the residue well washed with water and dried. The products obtained by this method were sufficiently pure for most purposes. The samples for analysis were crystallized from ethanol.

TABLE II.

Cinnamate prepared	*Yield per cent*	*m.p. °C.*	*Formula*	*ANALYSIS*				*Ref.*
				Found		*Calculated*		
				Per cent C	*Per cent H*	*Per cent C*	*Per cent H*	
Phenyl ..	90	74 – 75	$C_{15}H_{12}O_2$	80·46	5·44	80·33	5·40	5, 7, 10
o-Cresyl ..	91	84 – 85	$C_{16}H_{14}O_2$	80·73	6·03	80·65	5·92	8
m-Cresyl ..	90	65	$C_{16}H_{14}O_2$	80·60	5·95	80·65	5·92	9
p-Cresyl ..	86	100 – 101	$C_{16}H_{14}O_2$	80·84	5·83	80·65	5·92	7
α-Naphthyl ..	86	110 – 110·5	$C_{19}H_{14}O_2$	83·06	5·08	83·19	5·14	8
β-Naphthyl ..	93	101 – 102	$C_{19}H_{14}O_2$	83·26	5·20	83·19	5·14	7
*3-methoxyphenyl**	75	37 – 39	$C_{16}H_{14}O_3$	75·49	5·62	75·57	5·55	—

* *3-methoxyphenyl cinnamate* (b. p. 240 – 242/11 mm.) was also prepared from resorcinol monomethyl-ether and cinnamoyl chloride in the presence of pyridine. ($C_{16}H_{14}O_3$ requires 12·20 per cent OCH_3. Found: 12·5 per cent.). With bromine in acetic acid solution *3-methoxyphenyl-αβ-dibromohydrocinnamate*, m.p. 106°C.–108°C. is produced ($C_{16}H_{14}O_3Br_2$ requires Br, 38·6 per cent. Found: Br, 38·3 per cent.).

(*b*) *From cinnamic anhydride*

Cinnamic anhydride was obtained by adding concentrated sulphuric acid (1 drop) to a mixture of cinnamic acid (30 grams) and acetic anhydride (50 grams). The reaction mixture was boiled under reflux for one hour, and the excess of acetic anhydride and acetic acid was removed by distillation. The residue in the flask yielded colourless needles of cinnamic anhydride (25·4 grams; 91·4 per cent) m.p. 135°C. – 136°C. ($C_{18}H_{14}O_3$ requires C, 77·68 per cent; H, 5·07 per cent. Found: C, 77·53 per cent; H, 5·16 per cent.) (See also [8, 11, 12, 13, 14]). Phenolic cinnamates were obtained from cinnamic anhydride as follows:—

Concentrated sulphuric acid (1 drop) was added to an equimolecular mixture of cinnamic anhydride and the phenol. The mixture was heated in an oil-bath at 150°C. and poured into water when a white solid separated. The latter was triturated with a saturated solution of sodium bicarbonate, and the residue washed with water and dried. The product obtained by this method was sufficiently pure for most purposes.

The following phenolic cinnamates were prepared by this method: phenyl cinnamate (97 per cent yield), *o*-cresyl cinnamate (93 per cent yield), *m*-cresyl cinnamate (93 per cent yield) and *p*-cresyl cinnamate (92 per cent yield).

(*c*) *From cinnamic acid, and acetic anhydride*

Phenyl cinnamate: Concentrated sulphuric acid (1 drop) was added to an equimolecular mixture of cinnamic acid (2·3 grams), phenol (1·9 grams) and acetic anhydride (2·1 grams) when a rise in temperature of 30°C. was noticed. The mixture was then heated in an oil-bath for one hour at 150°C. and poured into water when a reddish oil separated, which smelled strongly of phenyl acetate. The mixture was carefully neutralized, and the phenyl acetate removed in a current of steam. After purification 1·9 grams of phenyl acetate were obtained, boiling at 185°C./625 mm. The non-volatile residue yielded phenyl cinnamate (1·3 grams, 2·9 per cent yield) and cinnamic acid (1·6 grams, 68 per cent recovery).

3-*Acetoxyphenyl cinnamate*: Concentrated sulphuric acid (10 drops) was added to an equimolecular mixture of resorcinol (27·5 grams) and cinnamic acid (37 grams) dissolved in acetic anhydride (50 grams). The temperature rose to 70°C., and the mixture was boiled under reflux for two and a half hours. On pouring into water a sticky orange-coloured solid separated, which after treatment with cold saturated sodium bicarbonate solution and ice-cold dilute sodium hydroxide gave 3-*acetoxyphenyl cinnamate* (27 grams; 40 per cent yield) melting at 80°C. – 83°C. Crystallization from ethanol (charcoal) gave colourless needles, m.p. 83·5°C. – 84·5°C. A mixed m.p. with a sample prepared from cinnamoyl chloride and resorcinol monoacetate showed no depression. ($C_{17}H_{14}O_4$ requires C, 72·33 per cent; H, 5·00 per cent. Found: C, 72·30 per cent; H, 5·08 per cent.) With bromine in glacial acetic acid 3-*acetoxyphenyl-αβ-dibromohydrocinnamate*, m.p. 122°C. – 123°C. is produced ($C_{17}H_{14}O_4Br_2$ requires Br, 36·20 per cent. Found: Br, 36·0 per cent.)

Reaction between cinnamic acid and phenyl acetate

Concentrated sulphuric acid (1 drop) was added to an equimolecular mixture of cinnamic acid (3 grams) and phenyl acetate (2·76 grams), and the reaction mixture was heated in an oil-bath for one hour. On pouring into water, a white solid separated, which on suitable treatment gave phenyl cinnamate (2·3 grams, 51 per cent yield) and cinnamic acid (1·0 gram, 33 per cent recovery). No phenyl acetate could be isolated from the reaction mixture.

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